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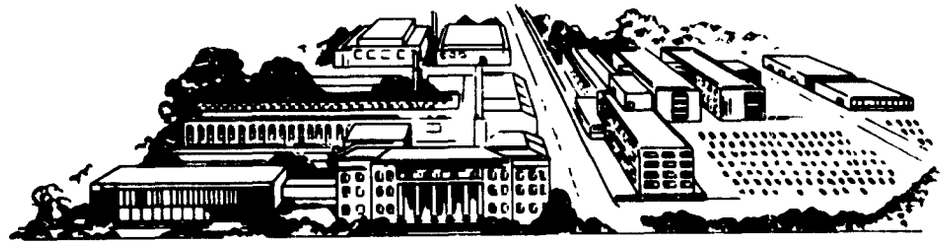
RESEARCH REPORT

DEVELOPMENT OF A DUCTILE
TUNGSTEN SHEET ALLOY

to

BUREAU OF NAVAL WEAPONS

May 26, 1962



BATTELLE
MEMORIAL INSTITUTE

SUMMARY REPORT

on

DEVELOPMENT OF A DUCTILE TUNGSTEN SHEET ALLOY

to

BUREAU OF NAVAL WEAPONS

May 26, 1962

by

J. L. Ratliff, D. J. Maykuth, H. R. Ogden,
and R. I. Jaffee

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ABSTRACT

This program was undertaken with the objective of improving the low-temperature ductility of tungsten by combining the principles of using dispersed oxides for grain-size control and high valency metal additions for matrix softening. Separate binary-alloy studies showed that increasing amounts of finely dispersed thoria or zirconia and critical amounts of rhenium, osmium, and iridium were effective in significantly reducing the ductile-to-brittle bend transition temperature of tungsten as well as in increasing its recrystallization temperature and decreasing its recrystallized grain size. Selected ternary alloys of rhenium, osmium, or iridium with thoria were then prepared. The beneficial effects shown by each of these additions on transition temperature and grain size in binary combinations appeared to be additive. Thus, combined additions of 2 to 8 volume per cent thoria with 5 per cent rhenium, 0.87 per cent osmium, or 0.30 per cent iridium were effective in lowering the transition temperature of tungsten from 200 C to 75 to 85 C, increasing its recrystallization temperature from 1600 C to 1800 C, and decreasing its recrystallized grain size.

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DEVELOPMENT OF A DUCTILE TUNGSTEN SHEET ALLOY

by

J. L. Ratliff, D. J. Maykuth, H. R. Ogden, and R. I. Jaffee

INTRODUCTION

This is a Summary Report on the "Development of a Ductile Tungsten Sheet Alloy" which describes the results of research performed over the period from April 26, 1961, through April 26, 1962.

The primary objective of this research was to develop tungsten-base sheet alloys having excellent fabricability and ductile-to-brittle transition temperatures below room temperature. Secondary objectives were the development of high recrystallization temperatures and high elevated-temperature strengths in these alloys.

The program proceeded by investigating separate binary-alloy combinations of tungsten with selected dispersoids, i.e., thoria and zirconia, and metallic additions of the Groups VII and VIII elements. Alloy compositions within these two groupings of materials, dispersoid and solid solution, were optimized to achieve maximum decreases in the transition temperature and maximum increases in the recrystallization temperature. From the results of this work, more complex dispersoid-solid solution alloys were designed, aimed at combining the separate beneficial effects of dispersoid and metallic additions.

SUMMARY

In the binary-dispersion-alloy studies, additions up through 12 volume per cent of thoria and zirconia were investigated. Thoria was added as an aqueous solution of thorium nitrate, while zirconia was added both as an aqueous solution of zirconium sulfate and as a 0.01-micron colloid. All of the thoriated alloys also contained a 0.2 weight per cent addition of Na_2O, while the zirconia alloys were prepared with and without the Na_2O addition.

It was shown that the fine dispersions of thoria and zirconia obtained appeared to have equivalent effects, on a volume per cent basis, on the fabricability, bend transition temperature, and recrystallization behavior of tungsten. The method of adding zirconia had no significant effects on end properties, although use of the colloid entailed less difficulty and gave results more consistent than those obtained with the aqueous salt.

Using the basic fabrication procedure adopted, the maximum amount of dispersed oxide permissible for obtaining good-quality 0.035-inch-thick strip was placed at about 8 volume per cent. This is equivalent to 4.4 weight per cent ThO_2 and 2.5 weight per cent ZrO_2, respectively.

Increasing amounts of thoria and zirconia were shown to be increasingly effective in decreasing the bend transition temperature of tungsten sheet in both the wrought (i.e., stress-relief annealed) and recrystallized conditions. Also, the choice of stress-relief annealing temperatures was shown to have a significant effect on the transition temperature of all wrought materials. For the 8 volume per cent dispersoid alloys, increasing the 1-hour stress-relief annealing temperature from 1000 C to 1300 C decreased bend transition temperatures by as much as 65 C. Minimum transition temperatures of 90 C and 85 C were obtained in the 8 volume per cent zirconia and thoria alloys, respectively. These values were 110 C to 115 C lower than the minimum transition temperature determined for an unalloyed tungsten control sample.

Increasing amounts of dispersed oxides also increased the recrystallization temperature of tungsten from 1600 C to values of 1800 C and 1900 C at the 8 volume per cent oxide level. Correspondingly, these alloys showed transition temperatures 75 to 90 C lower than those of unalloyed tungsten annealed at the same temperatures.

A series of arc-melted binary alloys of tungsten with 11 Group VII and VIII metals was prepared to verify and determine the magnitude of softening obtained in tungsten at small concentrations of these additions. The degree of softening afforded by individual additions was taken as a measure of the reduction in interstitial solubility, and analyses were later obtained to support this belief.

The greatest softening effects were obtained with alloying elements in the third long period, i.e., in alloys containing 0.30 atom per cent iridium, 0.87 atom per cent osmium, and 5 atom per cent rhenium which were increasingly effective (in the order listed) in decreasing the cast hardness of tungsten from 363 to 303 VHN.

Binary alloys containing these concentrations of rhenium, osmium, and iridium were successfully prepared as 0.035-inch thick strip using powder-metallurgical techniques. Each of these alloy additions was effective in increasing the recrystallization temperature and decreasing the recrystallized grain size of tungsten. Bend transition temperatures of these alloys were in the same relative order as predicted by their softening effects. Thus, the tungsten-rhenium alloy had the lowest transition temperatures, followed by the tungsten-osmium and tungsten-iridium alloys, in that order. The 5 per cent rhenium alloy showed transitions 35 C and 105 C lower than those obtained in unalloyed tungsten which were respectively obtained after stress-relief annealing and recrystallizing each material under comparable conditions.

A series of ternary alloys containing additions of 5 per cent rhenium, 0.87 per cent osmium, or 0.30 per cent iridium in combination with thoria in amounts through 8 volume per cent was then prepared. Fabrication of the ternary alloys containing 8 per cent thoria was more difficult than that of the binary alloys containing the same amount of thoria. Nevertheless, alloys of 5 per cent rhenium with 2 and 4 volume per cent thoria and of 0.87 per cent osmium and 0.30 per cent iridium with 8 volume per cent thoria were successfully rolled to 0.035-inch-thick strip.

Recrystallization temperatures of these ternary alloys were similar to those obtained with the individual binary metallic or thoria additions, i.e., about 200 C greater than the temperature of 1600 C obtained for unalloyed tungsten. However, the beneficial effects of the metallic and thoria additions on recrystallized grain size and transition temperature appeared to be additive in ternary combinations. Thus, the thoriated rhenium alloys showed finer grain sizes than were obtained with equivalent rhenium or thoria

additions alone. Also, the bend transition temperatures of the thoriated rhenium, osmium, and iridium alloys were the lowest obtained for any alloys in the program. Specifically, as stress-relief annealed, these alloys show ductile-to-brittle bend transition temperatures of 75 C to 85 C. These temperatures are 115 C to 125 C lower than those determined for the unalloyed tungsten-base material.

MATERIALS

A single 35-pound lot of unalloyed tungsten powder served as the base material for all of the unalloyed tungsten and tungsten alloys prepared and studied during this program. As reported in Table 1, the average particle size (Fisher No.) of this powder was 2.14 microns with a nominal purity of 99.93 per cent. Figure 1 illustrates a comparison made between the photelometric particle-size distributions of the powders selected for this program and that being used by the Fansteel Metallurgical Corporation in their Tungsten Sheet Rolling Program for the Navy.[1]* The distribution range representing the Fansteel material was found by them to offer a near optimum combination of good pressing, sintering, forging, and rolling characteristics. As can be seen from Figure 1, favorable comparison exists between this grade of material and that selected for this program.

TABLE 1. SUMMARY OF SUPPLIERS, PARTICLE SIZES, AND PURITIES OF ALL METAL POWDER MATERIALS

Material	Supplier	Average Particle Size[a], microns	Nominal Purity, wt %	Analysis, ppm							
				O	C	Mo	Ni	Fe	Ca	Si	Al
Tungsten	General Electric	2.14	99.93	560	10	10	<10	70	<10	<10	<10
Manganese	Charles Hardy	<74	99.0	--	--	--	--	--	--	--	--
Iron	Glidden	<74	99.85	700	180	20	80	--	--	70	20
Cobalt	Battelle, CIC	<74	99.92	--	70	--	50	100	--	--	--
Nickel	Sherritt-Gordon	<44	99.95	--	60	--	--	20	<10	<10	2
Ruthenium	Engelhard	<44	99.9	--	--	--	--	--	--	--	--
Rhodium	Engelhard	<44	99.8	--	--	--	--	--	--	--	--
Palladium	Engelhard	<44	99.9	--	--	--	--	--	--	--	--
Rhenium	Chase Brass	<74	99.99	--	--	35	--	12	1	<1	<1
Osmium	Engelhard	<44	99.6	--	--	--	--	--	--	--	--
Iridium	Engelhard	<44	99.8	--	--	--	--	--	--	--	--
Platinum	Engelhard	<44	99.9	--	--	--	--	--	--	--	--

(a) <74 and <44 designate powders which were -200 and -325 mesh, respectively.

As received, the entire powder lot was packaged in a single plastic bag sealed under an inert atmosphere. For ease of handling and to preserve both the initial purity and particle-size distribution, the entire lot was split by riffling into eight equal-size batches and stored under argon until needed.

The suppliers and the as-received analyses of the Groups VII and VIII metal powders purchased for this program are also given in Table 1. Each powder lot assayed at least 99.0 per cent pure and had a mesh size of -200, i.e., <74 microns, or finer.

*References are listed on page 80.

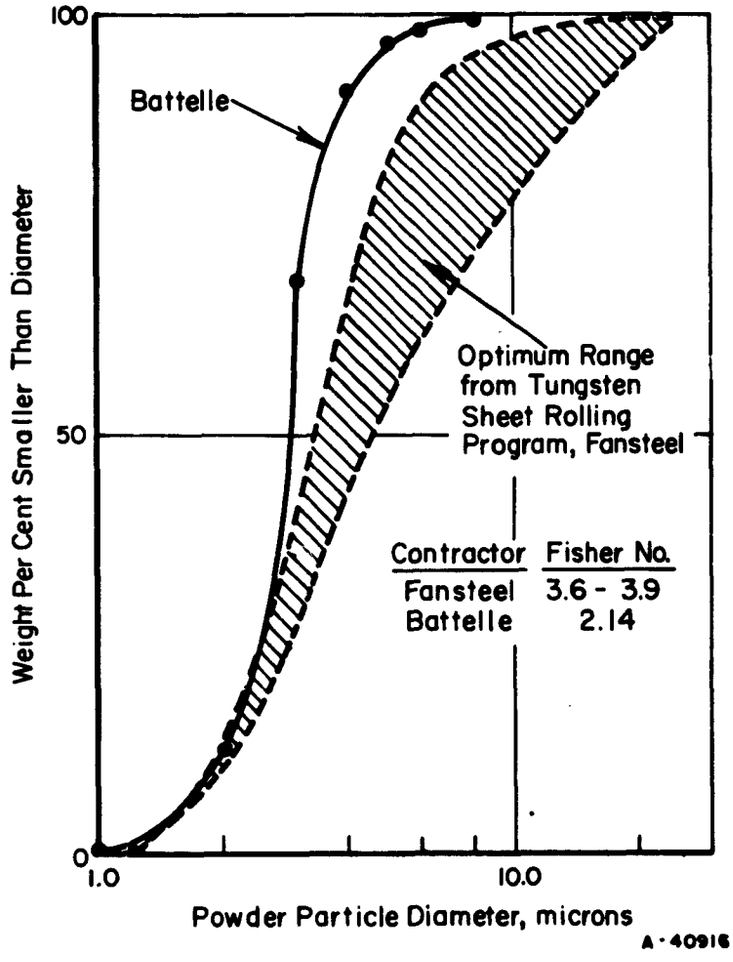


FIGURE 1. A COMPARISON BETWEEN THE POWDER PARTICLE-SIZE DISTRIBUTION USED IN THIS PROGRAM AND THE SIZE RANGE OPTIMIZED IN THE TUNGSTEN SHEET ROLLING PROGRAM

The principal oxides of interest to this program for dispersion applications were thoria, zirconia, and sodium oxide. Accordingly, supplies of $Th(NO_3)_4 \cdot 4H_2O$, $Zr(SO_4)_2 \cdot 4H_2O$, and NaCl were obtained from which aqueous preparations of dispersoid tungsten-base alloys could be effected. These salts assayed at least 98.0 per cent pure. In addition, a supply of zirconia sol, i.e., colloidal zirconia dispersed in water, was obtained which had an average particle size of 0.01 micron, reported by the supplier, and a nominal purity of 96.0 per cent.

DISPERSOID ALLOYS

Three groups of tungsten-base dispersoid alloys were investigated in this program. These groups are listed in Table 2 with their respective alloy compositions. As noted in this table, aqueous preparation from thorium nitrate was applied to all of the $W\text{-}ThO_2$ alloys. Compositions in this group ranged from 1 to 12 volume per cent thoria. Each $W\text{-}ThO_2$ alloy also contained 0.2 weight per cent sodium oxide, added as NaCl, since this additive was shown in previous work at Battelle[2] to be beneficial to the recrystallization characteristics of thoriated tungsten.

The two groups of $W\text{-}ZrO_2$ alloys listed in Table 2, one prepared aqueously from zirconium sulfate and the other from colloidal zirconia, spanned the 1 to 10 volume per cent and 1 to 12 volume per cent zirconia ranges, respectively. Additions of 0.2 weight per cent sodium oxide were also investigated in these alloys at the 1, 4, 8, and 10 volume per cent zirconia levels. Figure 2 relates weight per cent to volume per cent for both the $W\text{-}ThO_2$ and $W\text{-}ZrO_2$ alloy systems.

Compact Preparation and Sintering

The aqueous preparation of dispersoid alloys from thorium nitrate, zirconium sulfate, and NaCl was accomplished according to the following procedure: Appropriate quantities of the soluble salts were dissolved in 30 cubic centimeters of water and added to an unalloyed powder charge forming a slurry. Each charge was calculated to yield a total mass of 160 grams on the assumption that the residues from the aqueous additions would decompose thermally to form oxides in accordance with the following reactions:

$$Th(NO_3)_4 \cdot 4H_2O + 2NaCl \rightarrow \underline{ThO_2} + \underline{Na_2O} + 4HNO_3\uparrow + 2HCl\uparrow + H_2O\uparrow$$

$$Zr(SO_4)_2 \cdot 4H_2O \rightarrow \underline{ZrO_2} + 2SO_3\uparrow + 4H_2O\uparrow$$

$$Zr(SO_4)_2 \cdot 4H_2O + 2NaCl \quad \underline{ZrO_2} + \underline{Na_2O} + 2SO_3\uparrow + 2HCl\uparrow + 3H_2O\uparrow .$$

The water was removed by slowly evaporating the slurry on a hot plate while mixing the powder charge at frequent intervals. The resulting agglomerated powder mass was then broken up by light grinding with a mortar and pestle, cone blended by 1 hour, and finally stored in a drying oven at 200 F under an inert atmosphere prior to compaction.

Preparation of the $W\text{-}ZrO_2$ alloys from colloidal zirconia was accomplished in the following manner: Initially a precalculated amount of the zirconia sol, with or without

TABLE 2. SUMMARY OF DISPERSOID ALLOY COMPOSITIONS, SINTERING CONDITIONS, AND DENSITIES

Alloy	Nominal Alloy Content, Weight Per Cent	Nominal Alloy Content, Volume Per Cent	Sintering Conditions, Time, hr	Sintering Conditions, Temperature, C	Density, Theoretical[a], g/cm^3	Density, Per Cent of Theoretical, Initial[b]	Density, Per Cent of Theoretical, Final
			Unalloyed Tungsten				
W-1	100W	--	2	2600	19.30	56.5	93.8
W-2	100W	--	2	2600	19.30	56.3	93.0
W-3[c]	100W	--	4	2300	19.30	56.3	94.0
W-4	100W	--	2	2600	19.30	56.0	93.5
W-5	100W	--	2	2600	19.30	55.3	94.7
			Thoria Dispersoid Alloys Prepared From Aqueous Addditions				
WD-1	0.5ThO_2·0.2Na_2O	1ThO_2	2	2600		54.6	84.0
			2	2800	18.93	84.0	91.4
WD-11[d]	1.1ThO_2·0.2Na_2O	2ThO_2	2	2600	18.84	60.1	96.5
WD-12[d]	2.2ThO_2·0.2Na_2O	4ThO_2	2	2600	18.66	60.4	96.5
WD-4[d]	4.4ThO_2·0.2Na_2O	8ThO_2	2	2600	18.30	61.7	98.9
WD-13[d]	4.4ThO_2·0.2Na_2O	8ThO_2	2	2600	18.30	60.0	97.3
WD-35[e]	4.4ThO_2·0.2Na_2O	8ThO_2	2	2600	18.30	48.6	93.0
WD-42[e]	4.4ThO_2·0.2Na_2O	8ThO_2	2	2600	18.30	55.3	96.6
WD-43[e]	4.4ThO_2·0.2Na_2O	8ThO_2	2	2600	18.30	53.8	96.5
WD-40[e]	5.5ThO_2·0.2Na_2O	10ThO_2	2	2600	18.06	54.3	94.5
WD-41[e]	6.6ThO_2·0.2Na_2O	12ThO_2	2	2600	17.94	53.3	95.5
			Zirconia Dispersoid Alloys Prepared From Aqueous Additions				
WD-9	0.3ZrO_2·0.2Na_2O	1ZrO_2	2	2800	18.89	55.4	95.9
WD-14[d]	1.2ZrO_2	1ZrO_2	2	2600	18.75	58.0	99.7
WD-28[d]	1.2ZrO_2·0.2Na_2O	4ZrO_2	2	2600	18.48	55.0	94.7
WD-7[d]	2.5ZrO_2	8ZrO_2	2	2600	18.20	60.4	99.0
WD-15[d]	2.5ZrO_2	8ZrO_2	2	2600	18.20	59.8	100.0
WD-10[d]	2.5ZrO_2·0.2Na_2O	8ZrO_2	2	2600	17.95	60.0	103.0
WD-18[d]	3.1ZrO_2	10ZrO_2	2	2470	17.93	60.0	98.7
			Zirconia Dispersoid Alloys Prepared From 0.01-Micron Colloidal Zirconia				
WD-29	0.3ZrO_2	1ZrO_2	2	2600	19.16	57.2	94.3
WD-24	0.3ZrO_2·0.2Na_2O	1ZrO_2	2	2600	18.89	53.5	94.3
WD-20	1.2ZrO_2	4ZrO_2	2	2600	18.75	52.3	94.0
WD-25	1.2ZrO_2·0.2Na_2O	4ZrO_2	2	2600	18.48	53.4	96.4
WD-21	2.5ZrO_2	8ZrO_2	2	2600	18.20	54.8	96.5
WD-26	2.5ZrO_2·0.2Na_2O	8ZrO_2	2	2600	17.95	54.6	97.3
WD-37	2.5ZrO_2·0.2Na_2O	8ZrO_2	2	2600	17.95	52.6	94.0
WD-38	2.5ZrO_2·0.2Na_2O	8ZrO_2	2	2600	17.95	53.1	94.8
WD-39	2.5ZrO_2·0.2Na_2O	8ZrO_2	2	2600	17.95	53.8	100.0
WD-18	3.1ZrO_2	10ZrO_2	2	2600	17.93	55.3	97.6
WD-33	3.1ZrO_2·0.2Na_2O	10ZrO_2	2	2600	17.69	54.5	99.9
WD-23	3.8ZrO_2	12ZrO_2	2	2600	17.66	56.5	98.4

(a) Calculated using the relationship $\frac{1}{d} = \frac{wt\%A}{100d_a} + \frac{wt\%B}{100d_b} + \ldots$, where d values for ThO_2, ZrO_2, and Na_2O were taken as 10.03, 5.6, and 2.27 g/cm^3, respectively.

(b) After pressing under 50,000 psi and presintering for 2 hours in a dry hydrogen atmosphere.

(c) Vacuum radiation sintered prior to furnace-element burn out.

(d) Reprocessed alloys, see text.

(e) Prebaked alloys, see text.

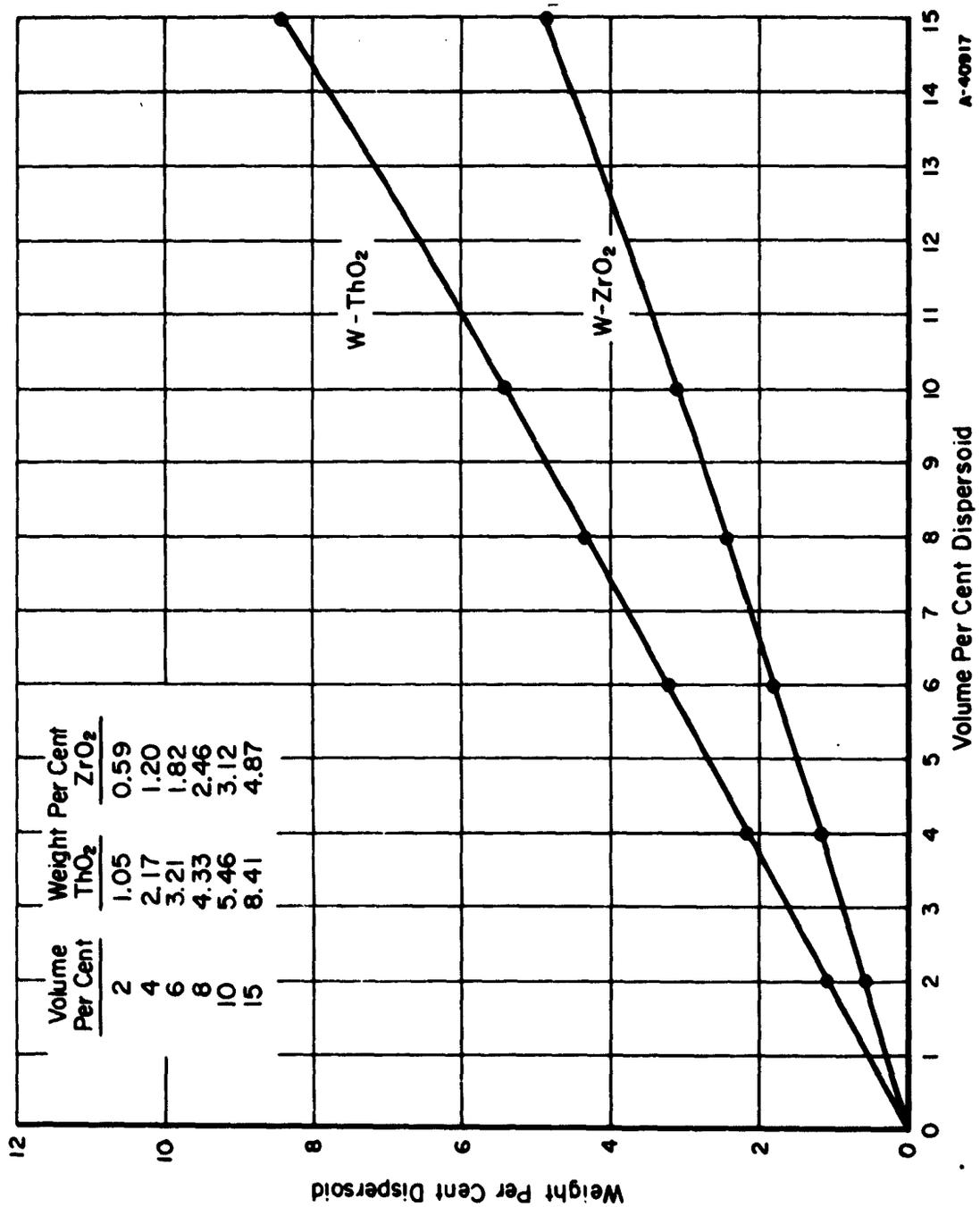


FIGURE 2. RELATION BETWEEN WEIGHT PER CENT AND VOLUME PER CENT FOR THE W-ThO_2 AND W-ZrO_2 ALLOYS

NaCl, was added to an unalloyed powder charge. This was followed by mixing, evaporating, grinding, blending, and storing in a manner similar to that described above for the aqueous-preparation technique.

Initial consolidation of the powder charges was carried out by mechanically pressing each into 1/4 x 1/2 x 7-inch bar under a peak pressure of 50,000 psi using a loading rate of 0.10 inch per minute. The resultant compacts were then presintered in a dried hydrogen atmosphere for 2 hours at 1200 C (2192 F). The intended purpose of this treatment was twofold. It served to complete the decomposition of any soluble salts present while simultaneously achieving sufficient compact green strength to allow handling prior to sintering.

Initial experiences with the dispersoid alloys prepared aqueously and containing greater than 1 volume per cent dispersion yielded compacts which either disintegrated during presintering or resulted in low presintered densities. These difficulties were associated with excessive gas evolution from decomposition of the soluble salts.

As a solution to this difficulty, all of the original compacts [Footnote (a), Table 2] were reprocessed by crushing, screening through -325 mesh, recompacting, and presintering. This alleviated the previous difficulties, as all of the presintered bars had excellent green strength and densities generally improved over these initially achieved.

During subsequent aqueous preparation of dispersoid alloys [Footnote (c), Table 2] a precompaction baking treatment was employed. This was carried out in a dried hydrogen atmosphere for 2 hours at 600 C (1112 F) and served to decompose the major portion of the soluble salts prior to presintering. The resultant presintered densities of the 34 powder bars prepared during this program and listed in Table 2 ranged from 48.6 to 61.7 per cent of theoretical.

Sintering of four of the five unalloyed tungsten bars and all 29 of the dispersoid alloys was carried out by self-resistance heating in vacuum. In the furnace used for this work, the ends of the presintered compacts were held in water-cooled copper grips and formed the resistance portion of a high-amperage, low-voltage circuit. The upper support grip was rigid, while the lower grip floated on a mercury contact pool to accommodate grip movement resulting for compact shrinkage during sintering.

Sintering temperatures were measured optically by sighting on the center-surface of each bar. True temperatures, T, were determined by the relationship

$$T = S + G + \Delta T,$$

where S is the apparent surface temperature (optical pyrometer value), G is the glass correction, and ΔT is the black-body temperature correction for tungsten using a wavelength of 0.655 micron.

Sintering was effected by heating each bar to 1000 C, outgassing for 1 hour, then heating to the sintering temperature over a period of 4 hours and holding at this temperature for 2 hours. Conditions used and resulting densities obtained are listed in Table 2. With only three exceptions the dispersoid alloys were sintered for 2 hours at 2600 C. This resulted in high-quality bars all of which had densities exceeding the minimum target density of 90 per cent of theoretical desired for subsequent good fabricability. Resulting densities ranged from 91.4 to 103 per cent of theoretical.

Both of the 1 volume per cent alloys of thoria and zirconia containing 0.2 weight per cent Na_2O which were not reprocessed or baked prior to compaction required more severe sintering conditions than 2 hours at 2600 C. In contrast, a third alloy, (WD-18, containing 10 volume per cent zirconia) was inadvertently sintered at 2470 C for 2 hours. Surprisingly, this bar still resulted in a final density of 98.7 per cent of theoretical, which suggested that a temperature appreciably lower than 2600 C could have been used in sintering many of these alloys.

Fabrication

The sintered bars of unalloyed tungsten and the dispersoid alloys were flat rolled to strip using the fabrication schedule presented in Table 3. Preheating was accomplished in a hydrogen tube furnace, and the rolling was performed on a 2-high mill equipped with 4 by 6-inch-wide rolls.

TABLE 3. FABRICATION SCHEDULE APPLIED TO THE DISPERSOID ALLOYS

Rolling Stage	Rolling Temperature, C	Rolling Temperature, F	Per Cent Reduction, Per Pass	Per Cent Reduction, Total	Annealing Temperature, C	Annealing Temperature, F	Annealing Time, min
Breakdown	1800	3272	15	29-43	--	--	--
Intermediate	1600	2912	10	18-31	1400	2552	30
Intermediate	1400	2552	10	35	1200	2192	30
Finish	1200	2192	10	36-41	--	--	--

The variable total reductions taken in the first two rolling stages at 1800 C and 1600 C, respectively, were designed to reduce the initial variable bar thicknesses to a uniform value. Thereafter, in the final rolling stages, a consistent rolling procedure was used. Variations in the per cent reductions taken during finish rolling were associated with the higher-dispersoid-content alloys which resisted deformation to a greater extent than did the lower-alloy-content strips.

Table 4 presents a qualitative summary of the behavior of unalloyed tungsten and all of the dispersoid alloys during rolling. The fabricability of each group of materials is discussed separately below.

Unalloyed Tungsten

As indicated in Table 4, all of the unalloyed-tungsten bars displayed excellent fabricability from initial breakdown rolling at 1800 C through finish rolling at 1200 C. Breakdown rolling and first-stage intermediate rolling at 1600 C resulted in coarse-grained structures, attributed to hot working of the material, while further rolling at 1400 C and 1200 C produced progressively more-heavily-fibered, wrought structures as illustrated in Figures 3(a and c) and 4(a and f).

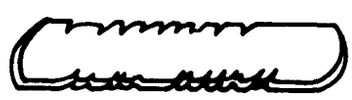
TABLE 4. QUALITATIVE SUMMARY OF BEHAVIOR OF UNALLOYED TUNGSTEN AND ALL OF THE DISPERSOID ALLOYS DURING ROLLING

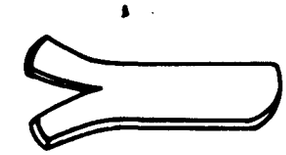
	Nominal Alloy Content		Quality of Strip[a]			
			Breakdown Rolling,	Intermediate Rolling		Finish Rolling,
Alloy	Weight Per Cent	Volume Per Cent	1800 C	1600 C	1400 C	1200 C
		Unalloyed Tungsten				
W-1	100W	100W	EC-1	E	E	E
W-2	100W	100W	E	E	E	E
W-3	100W	100W	E	E	E	E
W-4	100W	100W	E	E	E	E
W-5	100W	100W	E	E	E	E
	Thoria Dispersoid Alloys Prepared From Aqueous Additions					
WD-1	$0.5ThO_2 \cdot 0.2Na_2O$	$1ThO_2$	EC-1	E	E	E
WD-11	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	E	E	E	E
WD-12	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	E	E	E	E
WD-4	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	E	E	E	E
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	E	E	E	E
WD-35	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	L-3	--	--	--
WD-42	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	E	E	E	E
WD-43	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	E	E	E	E
WD-40	$5.5ThO_2 \cdot 0.2Na_2O$	$10ThO_2$	EC-1	EC-2	EC-2	LS-1 & EC-2
WD-41	$6.6ThO_2 \cdot 0.2Na_2O$	$12ThO_2$	L-3	--	--	--
	Zirconia Dispersoid Alloys Prepared From Aqueous Additions					
WD-9	$0.3ZrO_2 \cdot 0.2Na_2O$	$1ZrO_2$	E	E	E	E
WD-14	$1.2ZrO_2$	$4ZrO_2$	E	EC-1	EC-1	E
WD-28	$1.2ZrO_2 \cdot 0.2Na_2O$	$4ZrO_2$	EC-1	EC-1	EC-2	EC-1
WD-7	$2.5ZrO_2$	$8ZrO_2$	E	EC-1	EC-1	EC-1
WD-15	$2.5ZrO_2$	$8ZrO_2$	E	EC-1	EC-1	EC-1
WD-10	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	E	EC-1	EC-1	EC-1
WD-18	$3.1ZrO_2$	$10ZrO_2$	E	EC-1	EC-2	EC-3

TABLE 4. (Continued)

Alloy	Nominal Alloy Content, Weight Per Cent	Nominal Alloy Content, Volume Per Cent	Quality of Strip(a): Breakdown Rolling, 1800 C	Quality of Strip(a): Intermediate Rolling, 1600 C	Quality of Strip(a): Intermediate Rolling, 1400 C	Quality of Strip(a): Finish Rolling, 1200 C
Zirconia Dispersoid Alloys Prepared From 0.01-Micron Colloidal Zirconia						
WD-29	$0.3ZrO_2$	$1ZrO_2$	E	L-1	E	E
WD-24	$0.3ZrO_2 \cdot 0.2Na_2O$	$1ZrO_2$	E	E	E	E
WD-20	$1.2ZrO_2$	$4ZrO_2$	E	E	EC-1	E
WD-25	$1.2ZrO_2 \cdot 0.2Na_2O$	$4ZrO_2$	E	L-1	E	EC-1
WD-21	$2.5ZrO_2$	$8ZrO_2$	E	E	EC-1	EC-1
WD-26	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	E	E	EC-2	EC-1
WD-37	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	E	E	E	E
WD-38	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	E	EC-1 & L-1	E	E
WD-39	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	E	L-1	EC-1 & L-1	E
WD-22	$3.1ZrO_2$	$10ZrO_2$	E	E	EC-2	EC-2
WD-33	$3.1ZrO_2 \cdot 0.2Na_2O$	$10ZrO_2$	E	L-2	LS-3	--
WD-23	$3.8ZrO_2$	$12ZrO_2$	E	E	EC-2	LS-3

(a) E: Excellent
EC-1: Minor edge cracking
EC-2: Medium edge cracking
EC-3: Severe edge cracking and strip discarded
L-1: Minor lamination restricted to ends
L-2: Medium laminations
L-3: Severe laminations and strip discarded
LS-1: Minor longitudinal splitting restricted to ends
LS-2: Medium longitudinal splitting
LS-3: Severe longitudinal splitting and strip discarded





100X N83689

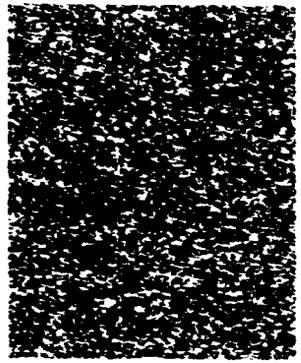
a. W-1: Unalloyed Tungsten, Rolled 1600 C, Annealed 1400 C

100X N83705

b. WD-1: 0.5ThO_2, 0.2Na_2O, Rolled 1600 C, Annealed 1400 C

100X N83708

c. WD-12: 1.1ThO_2, 0.2Na_2O, Rolled 1600 C, Annealed 1400 C



100X N83714

d. WD-13: 4.4ThO_2, 0.2Na_2O, Rolled 1600 C, Annealed 1400 C

100X N83688

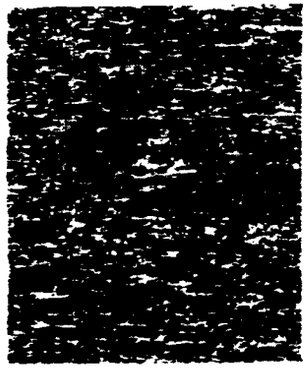
e. W-1: Unalloyed Tungsten, Rolled 1400 C, Annealed 1200 C

100X N83704

f. WD-1: 0.5ThO_2, 0.2Na_2O, Rolled 1400 C, Annealed 1200 C (1 Volume % ThO_2)

100X N83707

g. WD-12: 1.1 ThO_2, 0.2Na_2O, Rolled 1400 C, Annealed 1200 C (2 Volume % ThO_2)



100X N83713

h. WD-13: 4.4ThO_2, 0.2Na_2O, Rolled 1400 C, Annealed 1200 C (8 Volume % ThO_2)

FIGURE 3. LONGITUDINAL MICROSTRUCTURES ILLUSTRATING STRUCTURAL CHANGES OCCURRING DURING THE INTERMEDIATE FABRICATION STAGES OF UNALLOYED TUNGSTEN AND THREE THORIA DISPERSOID ALLOYS PREPARED FROM AQUEOUS ADDITIONS

Murakami's etch.

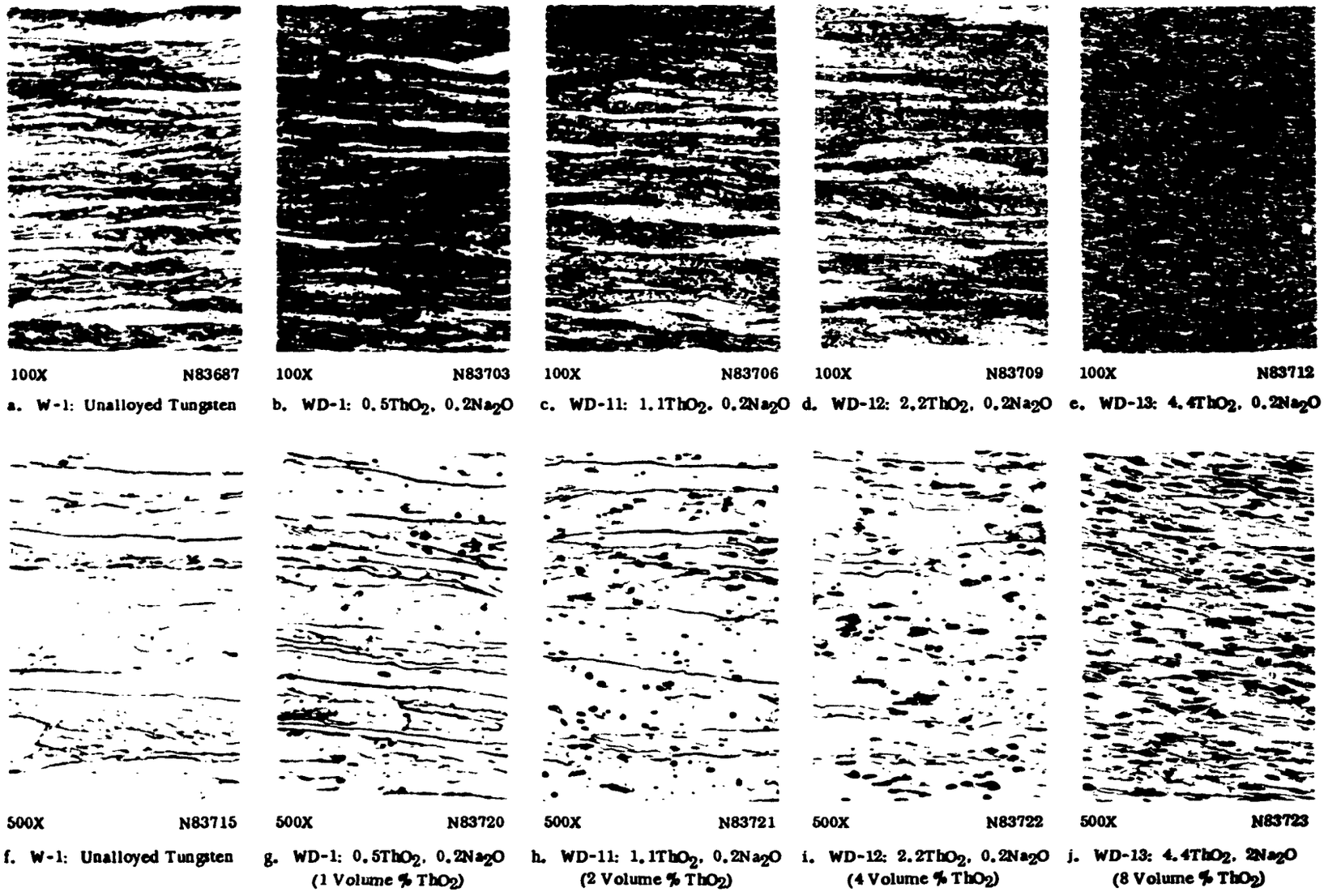


FIGURE 4. LONGITUDINAL MICROSTRUCTURES OF AS-WROUGHT UNALLOYED TUNGSTEN AND FOUR THORIA DISPERSOID ALLOYS PREPARED FROM AQUEOUS ADDITIONS, FINISH ROLLED AT 1200 C

Murakami's etch.

Tungsten-Thoria Alloys

The rolling behavior of the W-ThO_2·0.2Na_2O alloys was generally excellent through the 8 volume per cent level of thoria. At higher levels of thoria, fabricability was poor or impossible, indicating that the maximum amount of thoria for good fabricability (with the rolling conditions used) was about 8 volume per cent.

As illustrated in Figure 3, structural coarsening due to hot working occurred in the W-ThO_2 alloys through 4 volume per cent during breakdown and first-stage intermediate rolling. However, the degree of coarsening was diminished with increasing thoria content up to 4 volume per cent and was completely absent in the 8 volume per cent thoria alloy. After finish rolling, considerable refinement was obtained in the as-wrought microstructures of all of the W-ThO_2 alloys. Generally, as shown in Figure 4, the degree of fibering and uniformity of deformation increased with increasing thoria content.

Tungsten-Zirconia Alloys

Both groups of W-ZrO_2 alloys, i.e., one prepared from aqueous additions and the other from colloidal zirconia, displayed excellent fabricability during breakdown rolling at 1800 C. During subsequent fabrication from 1600 C through 1200 C, minor edge cracking predominated through the 8 volume per cent level of zirconia in the aqueously prepared group. Improved fabricability was displayed by the colloidal group of W-ZrO_2 alloys over the same range of rolling temperatures and compositions, as can be seen from Table 4. At higher zirconia contents than 8 volume per cent, the rolling performance in both alloy groups was very poor, thereby establishing 8 volume per cent as a fabricability limit in these alloys also. The presence of sodium oxide at any of the zirconia levels had no apparent effect on fabricability.

As previously described for the W-ThO_2 alloys, initial grain coarsening occurred during breakdown and first-stage intermediate rolling in both groups of W-ZrO_2 materials. Also, this tendency diminished with increasing zirconia content, but neither of the 8 volume per cent alloys prepared from either aqueous or colloidal additions was as effective in preventing this as the 8 volume per cent thoria alloy.

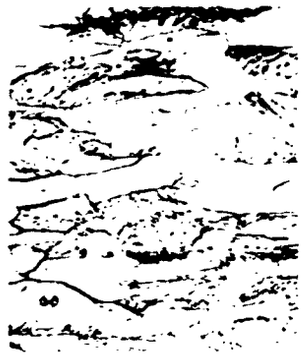
Figure 5 shows typical microstructures which illustrate the structural changes occurring in those W-ZrO_2 alloys prepared from colloidal zirconia after intermediate rolling at 1600 C and 1400 C. Microstructures (a through d of this figure) show the grain coarsening attributed to hot working during the early rolling stages. Figure 6 illustrates the as-wrought microstructures of these same alloys after finish rolling. As can be seen from these photomicrographs, increasing zirconia content also promoted more uniform deformation and considerable refinement of the as-wrought structures, as was the case with thoria.

Dispersoid-Alloy Compositions and Densities

Wrought samples of the 4 and 8 volume per cent alloys in each of the three groups of dispersoid alloys were analyzed gravimetrically for thoria and zirconia content. This work is summarized in Table 5 with the results indicating that 95 to 100 per cent of the zirconia and 85 to 90 per cent of the thoria were retained after sintering.

100X N84983

a. W-4 Unalloyed Tungsten, Rolled 1600 C, Annealed 1400 C



100X N84986

b. WD-29 W-0.3ZrO_2, Rolled 1600 C, Annealed 1400 C

100X N84989

c. WD-20 W-1.2ZrO_2, Rolled 1600 C, Annealed 1400 C

100X N84992

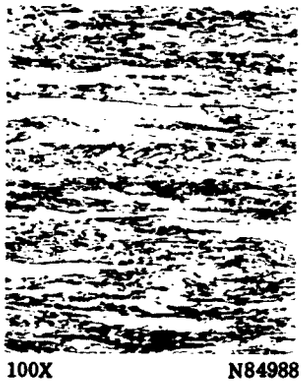
d. WD-21 W-2.5ZrO_2, Rolled 1600 C, Annealed 1400 C

100X N84982

e. W-4 Unalloyed Tungsten, Rolled 1400 C, Annealed 1200 C

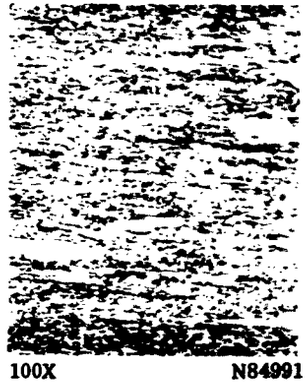
100X N84985

f. WD-9 W-0.3ZrO_2, Rolled 1400 C, Annealed 1200 C (1 Volume % ZrO_2)



100X N84988

g. WD-20 W01.2ZrO_2 Rolled 1400 C, Annealed 1200 C (4 Volume % ZrO_2)



100X N84991

h. WD-21 W-2.5ZrO_2 Rolled 1400 C, Annealed 1200 C (8 Volume % ZrO_2)

FIGURE 5. LONGITUDINAL MICROSTRUCTURES ILLUSTRATING STRUCTURAL CHANGES OCCURRING DURING THE INTERMEDIATE FABRICATION STAGES OF UNALLOYED TUNGSTEN AND THREE ZIRCONIA DISPERSOID ALLOYS PREPARED FROM COLLOIDAL ZIRCONIA

Murakami's etch.

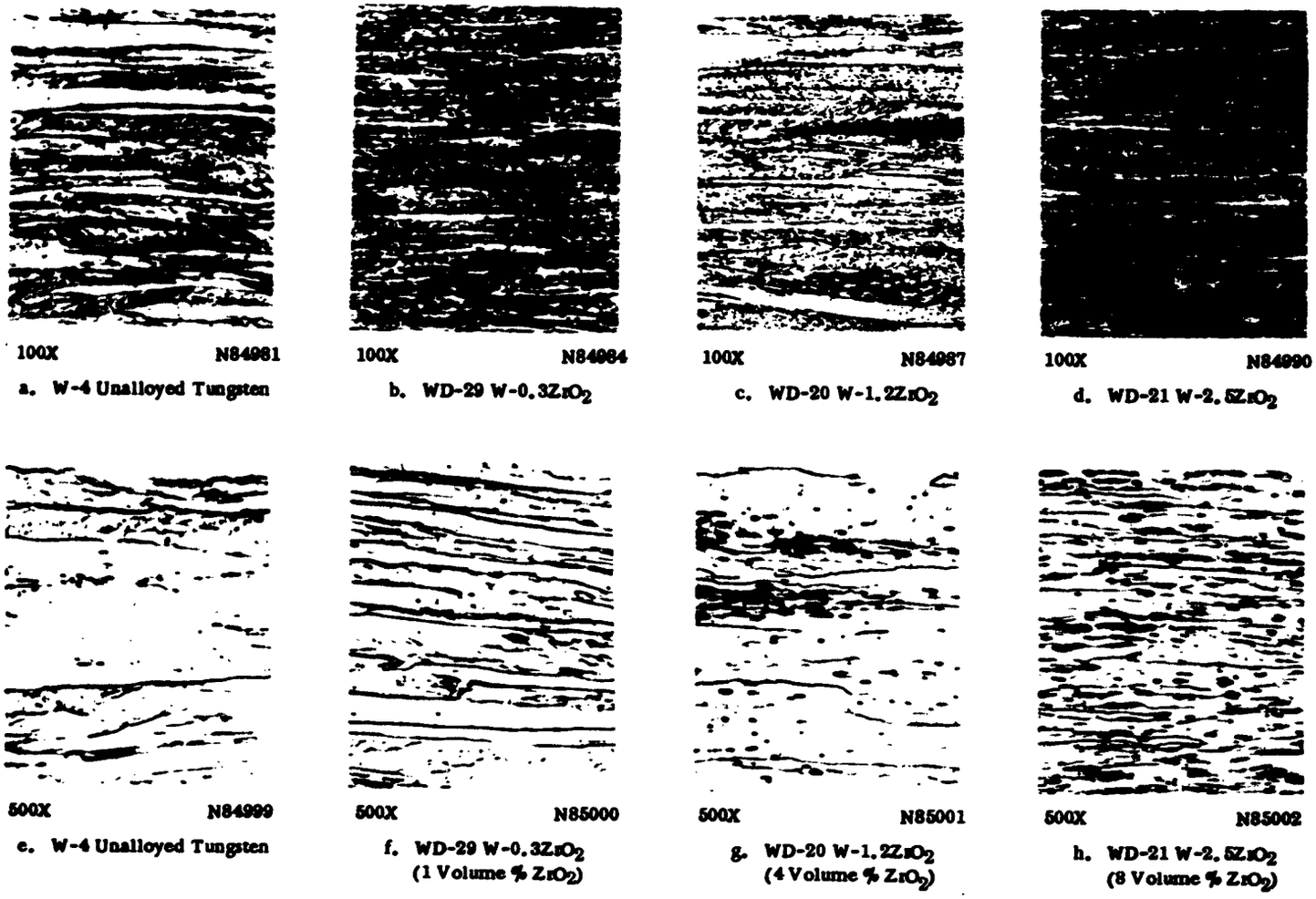


FIGURE 6. LONGITUDINAL MICROSTRUCTURES OF AS-WROUGHT UNALLOYED TUNGSTEN AND THREE ZIRCONIA DISPERSOID ALLOYS PREPARED FROM COLLOIDAL ZIRCONIA, FINISH ROLLED AT 1200 C

Murakami's etch.

TABLE 5. SUMMARY OF ANALYTICAL DATA AND EXPERIMENTAL DENSITY DETERMINATIONS ON WROUGHT UNALLOYED TUNGSTEN AND SELECTED DISPERSOID ALLOYS

Alloy	Alloy Content, weight per cent		Density, g/cm^3		Per Cent Deviation
	Nominal	Analyzed[a]	Theoretical	Measured[c]	
Unalloyed Tungsten					
W-1	100W	--	19.30	19.45	+0.77
Thoria Dispersoid Alloys Prepared From Aqueous Additions					
WD-1	$0.5ThO_2 \cdot 0.2Na_2O$	--	18.93	19.49	+2.95
WD-11	$0.1ThO_2 \cdot 0.2Na_2O$	--	18.84	18.97	+0.69
WD-12	$2.2ThO_2 \cdot 0.2Na_2O$	$1.90ThO_2$	18.66[b]	18.98	+1.72
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$	$3.97ThO_2$	18.35[b]	18.61	+1.42
Zirconia Dispersoid Alloys Prepared From Aqueous Additions					
WD-28	$1.2ZrO_2 \cdot 0.2Na_2O$	$1.24ZrO_2$	18.46[b]	18.81	+1.90
WD-10	$2.5ZrO_2 \cdot 0.2Na_2O$	$2.36ZrO_2$	17.99[b]	18.40	+2.28
Zirconia Dispersoid Alloys Prepared From 0.01-Micron Colloidal Zirconia					
WD-29	$0.3ZrO_2$	--	19.16	19.18	+0.10
WD-24	$0.3ZrO_2 \cdot 0.2Na_2O$	--	18.89	19.35	+2.44
WD-20	$1.2ZrO_2$	--	18.75	18.61	-0.75
WD-25	$1.2ZrO_2 \cdot 0.2Na_2O$	$1.36ZrO_2$	18.41[b]	18.66	+1.36
WD-21	$2.5ZrO_2$	--	17.95	18.11	+0.89
WD-26	$2.5ZrO_2 \cdot 0.2Na_2O$	$2.45ZrO_2$	17.95[b]	18.36	+2.28
WD-22	$3.1ZrO_2$	--	17.93	18.01	+0.45

(a) An average of duplicate gravimetric determinations made on randomly selected 1-gram samples.

(b) Calculated on the basis of analyzed alloy content.

(c) Determined experimentally by water-displacement technique.

Densities were measured by water displacement on the 14 representative wrought samples listed in Table 5. These densities were compared with their theoretical values through a calculation of per cent deviation from the theoretical. In all instances except one, the deviations of the measured values from the theoretical were positive.

Although none of the alloys were analyzed to determine sodium oxide content after sintering, a statistical inference drawn from the density measurements indicated Na_2O to be low. Loss of sodium oxide would lead to a greater measured density than the theoretical and hence a greater positive deviation than normally expected from experimental error. This phenomenon was observed as shown in Table 5. The average per cent deviation for those alloys containing sodium oxide was $+1.89 \pm 0.68$, while that for those alloys without sodium oxide was $+0.35 \pm 0.66$.

Softening, Recrystallization, and Grain-Growth Behaviors

Softening and recrystallization studies were carried out on wrought samples of unalloyed tungsten and all of the dispersoid alloys.

Samples of the alloys were annealed for 1 hour at temperatures from 1000 C through 2300 C, and the resultant microstructures were examined for evidence of recrystallization.

After each alloy was annealed and examined, the Vickers hardness was determined. This work is summarized in Table 6 which also includes hardness data from samples of all the materials after intermediate and finish rolling. During fabrication the hardnesses of the alloys increased progressively. Comparisons of as-wrought hardness values after finish rolling at 1200 C showed the higher level dispersed alloys to be 20 to 50 VHN harder than the lower level alloys.

Figures 7 through 9 illustrate the softening characteristics for all three groups of the dispersoid alloys. Shown in these figures are unalloyed tungsten and the 1, 4, and 8 volume per cent dispersoid levels (with 0.2 weight per cent Na_2O added) for each of the three dispersoid groups. Generally, the shapes of all the softening curves were similar. Hardness levels remained relatively constant or increased slightly with increasing annealing temperatures up to 1200 C, then dropped off rapidly over the range 1400 C to 1800 C. At higher temperatures, the hardnesses leveled off and approached a constant value. With few exceptions, the hardness values of the higher level dispersoid alloys remained consistently higher than those of the lower level alloys over the entire range of annealing temperatures.

The beginning and finish of recrystallization is denoted on each curve in Figures 7 through 9 by S and F and a summary of these data is presented in Table 7. For unalloyed tungsten the temperature range for 1-hour recrystallization spanned 200 degrees between 1400 C(S) and 1600 C(F). Recrystallization also began at 1400 C for the 1, 4, and 8 volume per cent W-ThO_2 alloys but finished at 1600 C, 1700 C, and 1900 C, respectively. Thus, the general effect of increasing thoria content was to raise the recrystallization temperature and extend the range over which it occurred. As compared with thoria, the 1, 4, and 8 volume per cent levels of zirconia in both groups of W-ZrO_2 alloys did not tend to extend the temperature range over which recrystallization occurred. Instead, the zirconia additions tended to raise both the starting and finishing temperatures of recrystallization by 200 degrees to 1600 C and 1800 C, respectively. From this work it is significant to note that the highest 1-hour temperature for complete recrystallization, 1900 C, was observed for the 8 volume per cent thoria alloy. This may be compared with 1600 C for unalloyed tungsten and a common value of 1800 C for all of the W-ZrO_2 alloys containing greater than 1 volume per cent zirconia.

The grain size of each recrystallized microstructure resulting from the softening and recrystallization studies was determined by the line-intercept counting technique and

TABLE 6. EFFECT OF FABRICATION AND ANNEALING ON THE MICROHARDNESS OF UNALLOYED TUNGSTEN AND THE DISPERSOID ALLOYS

Alloy	Nominal Alloy Content, Weight Per Cent	Nominal Alloy Content, Volume Per Cent	Vickers Hardness Numbers (VHN), 10-Kg Load: Rolled 1600 C, Annealed 1400 C	Rolled 1400 C, Annealed 1200 C	As-Wrought Rolled 1200 C	1-Hour Vacuum Annealing Temperature, C: 1000	1200	1300	1400	1500	1600	1700	1800	1900	2000	2300
Unalloyed Tungsten																
W-1	100W	100W	457	485	508	504	493	--	387	376	380(a)	--	380(a)	--	371(a)	363(a)
W-4	100W	100W				484	496	485	459	--	379(a)	--	358(a)	--	357(a)	--
Thoria Dispersoid Alloys Prepared From Aqueous Additions																
WD-1	$0.5ThO_2 \cdot 0.2Na_2O$	$1ThO_2$	442	468	500	494	496	--	461	425	379(a)	--	354(a)	--	378(a)	366(a)
WD-11	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	446	493	507	492	506	--	483	--	418	397(a)	381(a)	--	383(a)	383(a)
WD-12	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	446	498	502	521	504	--	480	--	438	401(a)	409(a)	--	400(a)	390(a)
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	459	508	553	559	566	--	535	--	431	--	444	429(a)	441(a)	409(a)
Zirconia Dispersoid Alloys Prepared From Aqueous Additions																
WD-9	$0.3ZrO_2 \cdot 0.2Na_2O$	$1ZrO_2$	464	498	510	518	507	--	488	--	427	--	396(a)	--	388(a)	--
WD-14	$1.2ZrO_2$	$4ZrO_2$	478	488	515	533	520	--	514	--	456	--	411(a)	--	405(a)	--
WD-28	$1.2ZrO_2 \cdot 0.2Na_2O$	$4ZrO_2$	--	--	516	520	518	--	492	--	432	--	412(a)	--	405(a)	--
WD-7	$2.5ZrO_2$	$8ZrO_2$	459	493	530	514	531	--	524	--	487	--	428(a)	--	414(a)	--
WD-10	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	--	--	540	545	530	--	500	--	424	--	436(a)	--	434(a)	--
WD-18	$3.1ZrO_2$	$10ZrO_2$	473	508	538	553	534	--	509	--	436	--	424(a)	--	439(a)	--
Zirconia Dispersoid Alloys Prepared From 0.01-Micron Colloidal Zirconia																
WD-29	$0.3ZrO_2$	$1ZrO_2$	466	489	518	507	495	--	475	--	383	380(a)	378(a)	--	377(a)	370(a)
WD-24	$0.3ZrO_2 \cdot 0.2Na_2O$	$1ZrO_2$	--	--	510	502	500	--	488	--	419	390(a)	378(a)	--	385(a)	376(a)
WD-20	$1.2ZrO_2$	$4ZrO_2$	465	484	495	519	512	--	507	--	462	446	394(a)	--	389(a)	409(a)
WD-25	$1.2ZrO_2 \cdot 0.2Na_2O$	$4ZrO_2$	--	--	502	515	510	--	500	--	467	442	400(a)	--	399(a)	402(a)
WD-21	$2.5ZrO_2$	$8ZrO_2$	474	473	--	526	531	--	508	--	507	459	450(a)	--	431(a)	417(a)
WD-26	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	--	--	534	541	528	--	514	--	497	478	428(a)	--	432(a)	425(a)
WD-22	$3.1ZrO_2$	$10ZrO_2$	496	493	540	536	529	--	513	--	499	483	450(a)	--	440(a)	437(a)
WD-23	$3.8ZrO_2$	$12ZrO_2$	486	509	530	--	544	--	--	--	--	--	439(a)	--	437(a)	--

(a) Fully recrystallized microstructures

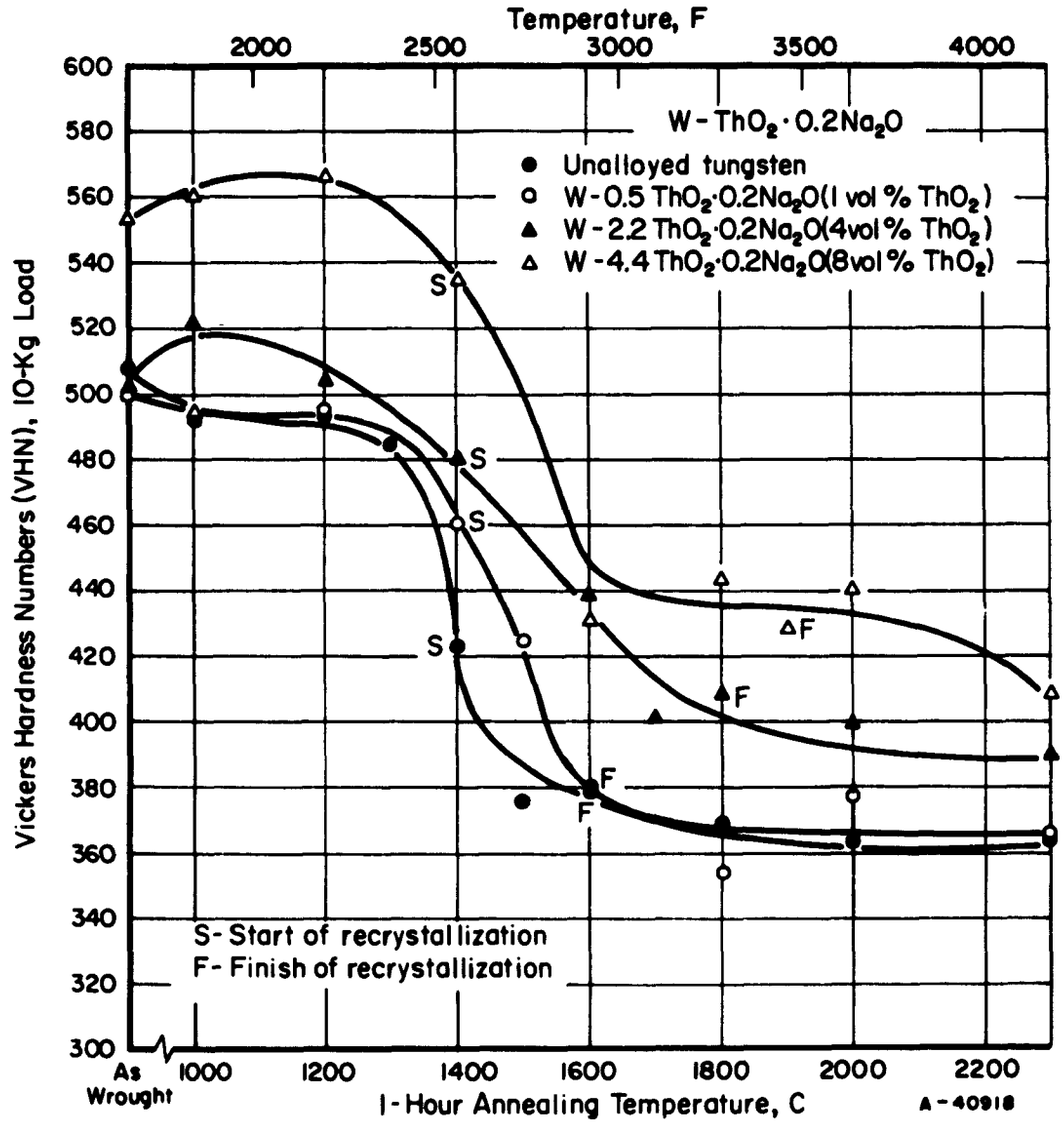


FIGURE 7. SOFTENING CURVES FOR WROUGHT UNALLOYED TUNGSTEN AND THE 1, 4, AND 8 VOLUME PER CENT THORIA DISPERSOID ALLOYS PREPARED FROM AQUEOUS ADDITIONS

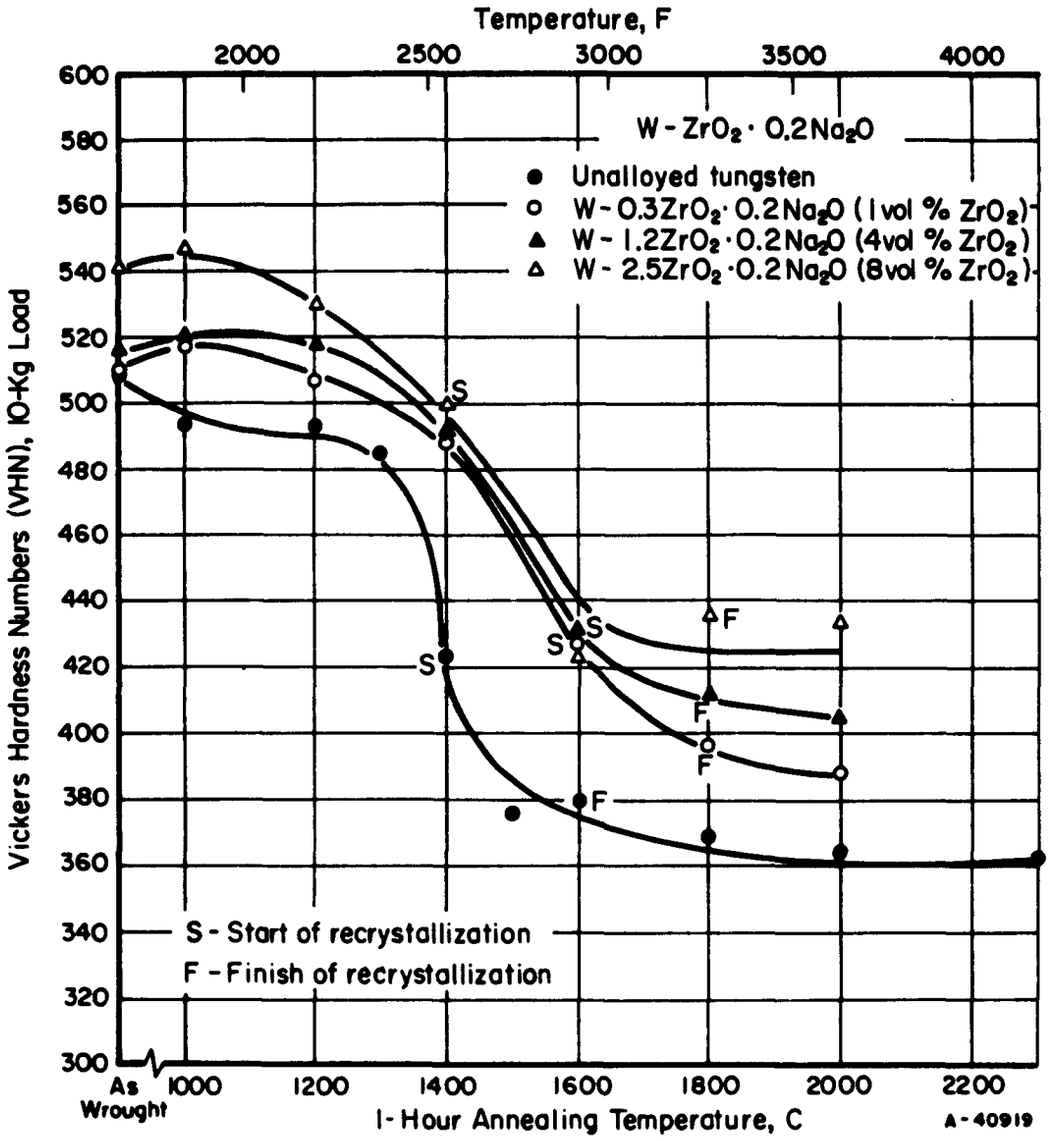


FIGURE 8. SOFTENING CURVES FOR WROUGHT UNALLOYED TUNGSTEN AND THE 1, 4, AND 8 VOLUME PER CENT ZIRCONIA DISPERSOID ALLOYS PREPARED FROM AQUEOUS ADDITIONS

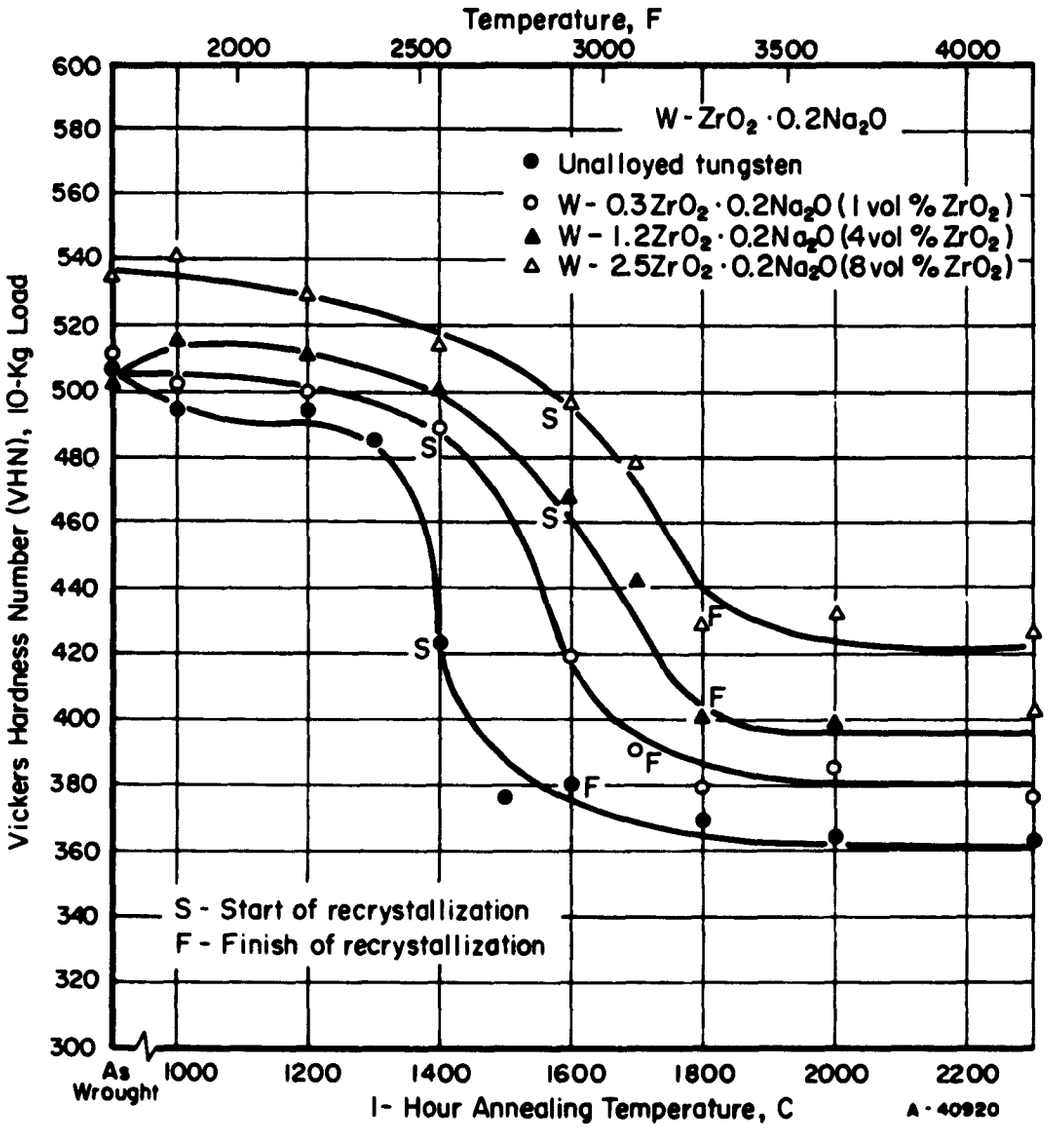


FIGURE 9. SOFTENING CURVES FOR WROUGHT UNALLOYED TUNGSTEN AND THE 1, 4, AND 8 VOLUME PER CENT ZIRCONIA DISPERSOID ALLOYS PREPARED FROM 0.01-MICRON COLLOIDAL ZIRCONIA

TABLE 7. SUMMARY OF RECRYSTALLIZATION OBSERVATIONS MADE ON UNALLOYED TUNGSTEN AND THE 1, 4, AND 8 VOLUME PER CENT DISPERSOID ALLOYS

Alloy	Nominal Alloy Content		1-Hr Recrystallization Temperature, C		Recrystallization Range, Δ C
	Weight Per Cent	Volume Per Cent	Start (S)	Finish (F)	
WD-1	100W	100W	1400	1600	200
WD-1	$0.5ThO_2 \cdot 0.2Na_2O$(Aq.)	$1ThO_2$	1400	1600	200
WD-12	$2.2ThO_2 \cdot 0.2Na_2O$(Aq.)	$4ThO_2$	1400	1800	400
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$(Aq.)	$8ThO_2$	1400	1900	500
WD-9	$0.3ZrO_2 \cdot 0.2Na_2O$(Aq.)	$1ZrO_2$	1600	1800	200
WD-28	$1.2ZrO_2 \cdot 0.2Na_2O$(Aq.)	$4ZrO_2$	1600	1800	200
WD-10	$2.5ZrO_2 \cdot 0.2Na_2O$(Aq.)	$8ZrO_2$	1400	1800	400
WD-24	$0.3ZrO_2 \cdot 0.2Na_2O$(Col.)	$1ZrO_2$	1400	1700	300
WD-25	$1.2ZrO_2 \cdot 0.2Na_2O$(Col.)	$4ZrO_2$	1600	1800	200
WD-26	$2.5ZrO_2 \cdot 0.2Na_2O$(Col.)	$8ZrO_2$	1600	1800	200

reported as grains per square millimeter. These data, along with the approximate 1-hour recrystallization temperature of each alloy, are tabulated in Table 8. The results of this work are discussed below.

Tungsten-Thoria Alloys

Figure 10 illustrates the effect of increasing thoria content on recrystallized grain size for annealing temperatures of 1800 C, 2000 C, and 2300 C. From the curves shown, it is evident that increasing thoria content promoted successively finer-grained structures than were possible with unalloyed tungsten. The finest grain sizes in this series of materials were displayed by the 8 volume per cent W-ThO_2 alloy. After annealing at 1900 C, this alloy showed 6800 grains/mm^2. Comparisons with unalloyed tungsten were possible at 2000 C and 2300 C, where the 8 volume per cent alloy showed 6300 and 5000 grain/mm^2, respectively, while averages of 713 and 175 grains/mm^2 were noted for unalloyed tungsten.

Figure 11 illustrates the effect of increasing annealing temperature on the resultant grain sizes of unalloyed tungsten and the 1, 4, and 8 volume per cent W-ThO_2 alloys. As shown, the slope of each curve in this figure is essentially the same; thus, none of the materials showed significantly different rates of grain growth. From this it was concluded that the effectiveness of thoria dispersions in producing fine-grained recrystallized structures is more dependent on their grain-refining characteristics during both rolling and annealing than on their ability to retard grain growth after recrystallization.

Tungsten-Zirconia Alloys

The effect of increasing zirconia content on recrystallized grain size is shown in Figures 12 and 13. From the curves shown, it is evident that zirconia additions also influence grain size. However, the effect of zirconia is not as clearly defined as that previously described for thoria.

The grain-refining characteristics of zirconia added through aqueous preparation are shown in Figure 12. A classification of the alloys in this group as to whether or not they contained a 0.2 weight per cent addition of Na_2O resulted in several interesting phenomena. Fluctuations occurred in the grain-refining characteristics of both classes, as those compositions without Na_2O displayed maximum refinement at 8 volume per cent with 6000 grains/mm^2, while minimal refinement occurred at 4 volume per cent for those alloys containing Na_2O. Another interesting property of this series of W-ZrO_2 alloys was the reversal in grain-refining effectiveness which occurred for the alloys with and without Na_2O added. At zirconia levels greater than 2.5 volume per cent the alloys without Na_2O produced superior refinement.

TABLE 8. SUMMARY OF RECRYSTALLIZATION TEMPERATURES AND THE EFFECT OF HIGH TEMPERATURE ANNEALING ON THE GRAIN SIZE ON UNALLOYED TUNGSTEN AND THE TUNGSTEN-BASE DISPERSOID ALLOYS

Alloy	Nominal Alloy Content, Weight Per Cent	Nominal Alloy Content, Volume Per Cent	Approximate 1-Hr Recrystallization Temperature, C	Grain Size as Determined by Line-Intercept Technique, grains/mm^2 — 1-Hour Vacuum Annealing Temperature, C: 1600	1700	1800	1900	2000	2300
Unalloyed Tungsten									
W-1	100W	100W	1600	1000	--	1175	--	650	--
W-4	100W	100W	1600	975	--	1150	--	775	175
Thoria Dispersoid Alloys Prepared From Aqueous Additions									
WD-1	$0.5ThO_2 \cdot 0.2Na_2O$	$1ThO_2$	1600	1450	--	1425	--	700	600
WD-11	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	1700	--	1950	2125	--	1150	900
WD-12	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	1700	--	2850	2900	--	1875	900
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	1900	--	--	--	6800	6300	5000
Zirconia Dispersoid Alloys Prepared From Aqueous Additions									
WD-9	$0.3ZrO_2 \cdot 0.2Na_2O$	$1ZrO_2$	1800	--	--	3200	--	2675	--
WD-14	$1.2ZrO_2$	$4ZrO_2$	1800	--	--	3525	--	3525	--
WD-28	$1.2ZrO_2 \cdot 0.2Na_2O$	$4ZrO_2$	1800	--	--	2200	--	1875	--
WD-7	$2.5ZrO_2$	$8ZrO_2$	1800	--	--	6000	--	3850	--
WD-10	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	1800	--	--	4800	--	2650	--
WD-18	$3.1ZrO_2$	$10ZrO_2$	1800	--	--	3900	--	2800	--
Zirconia Dispersoid Alloys Prepared From 0.01-Micron Colloidal Zirconia									
WD-29	$0.3ZrO_2$	$1ZrO_2$	1700	--	1450	1300	--	750	425
WD-24	$0.3ZrO_2 \cdot 0.2Na_2O$	$1ZrO_2$	1700	--	1275	1675	--	925	600
WD-20	$1.2ZrO_2$	$4ZrO_2$	1800	--	--	2650	--	1450	1375
WD-25	$1.2ZrO_2 \cdot 0.2Na_2O$	$4ZrO_2$	1800	--	--	2625	--	1800	875
WD-21	$2.5ZrO_2$	$8ZrO_2$	1800	--	--	8900	--	5800	5000
WD-26	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	1800	--	--	6400	--	5600	3700
WD-22	$3.1ZrO_2$	$10ZrO_2$	1800	--	--	9250	--	9000	8400

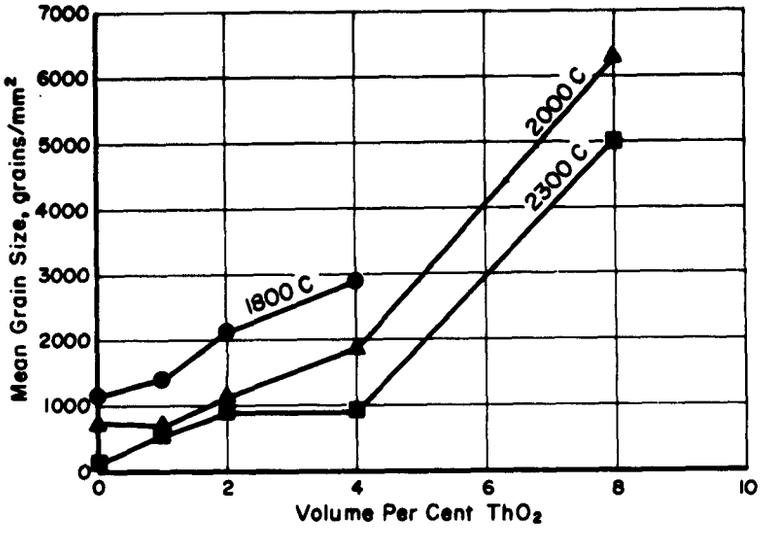


FIGURE 10. EFFECT OF INCREASING THORIA CONTENT ON THE RECRYSTALLIZED GRAIN SIZE OF THE THORIA DISPERSOID ALLOYS PREPARED FROM AQUEOUS ADDITIONS AND ANNEALED FOR 1 HOUR AT THE INDICATED TEMPERATURES

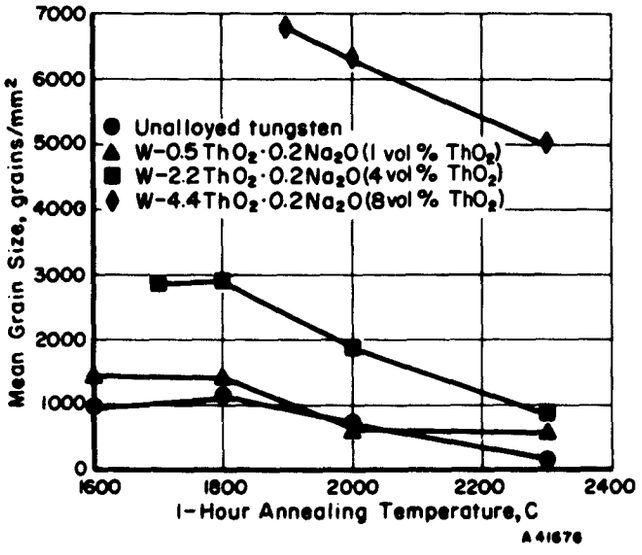


FIGURE 11. GRAIN-GROWTH BEHAVIOR OF UNALLOYED TUNGSTEN AND THE 1, 4, AND 8 VOLUME PER CENT THORIA DISPERSOID ALLOYS PREPARED FROM AQUEOUS ADDITIONS

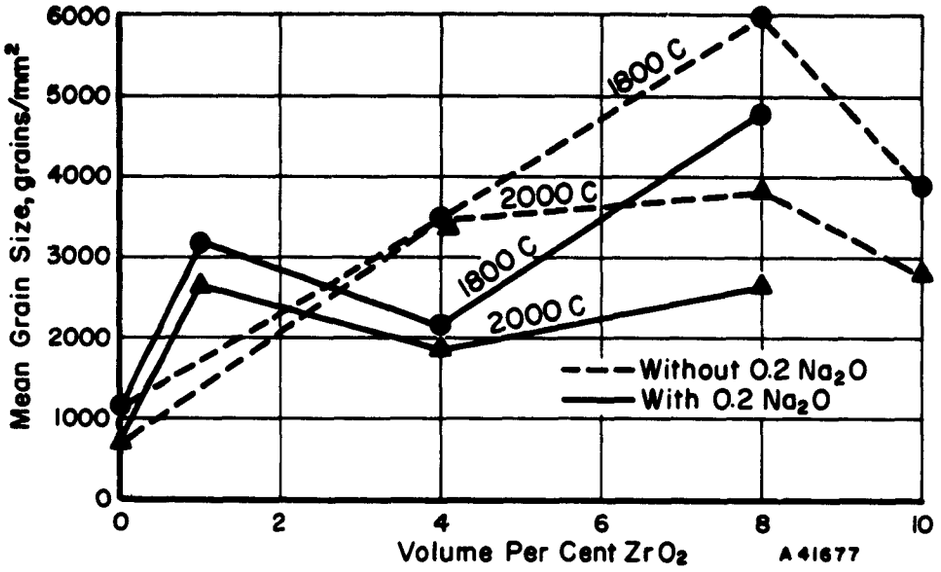


FIGURE 12. EFFECT OF INCREASING ZIRCONIA CONTENT ON THE RECRYSTALLIZED GRAIN SIZE OF THE ZIRCONIA DISPERSOID ALLOYS PREPARED FROM AQUEOUS ADDITIONS AND ANNEALED FOR 1 HOUR AT THE INDICATED TEMPERATURES

The grain-refining characteristics of zirconia added through colloidal preparation are illustrated in Figure 13. As with the aqueously prepared zirconia alloys, these alloys also showed reversals in grain-refinement effectiveness at the lower zirconia contents. Thus, above a certain volume per cent level of zirconia for each annealing temperature shown, those alloys not containing Na_2O resulted in the finer-grained structures. More specifically, the reversals occurred at approximately 4, 8, and 2 volume per cent zirconia for the respective annealing temperatures of 1800 C, 2000 C, and 2300 C.

Figure 14 illustrates the effect of increasing 1-hour annealing temperatures on the resulting grain sizes of unalloyed tungsten and the W-ZrO_2 alloys prepared from colloidal zirconia. As indicated by the similarity in slope of these curves, none of the alloys showed significantly different rates of grain growth. Thus, as with thoria, the effectiveness of zirconia in producing fine-grained recrystallized structures is primarily dependent on its grain-refining characteristics rather than on its ability to retard grain growth after recrystallization.

The nominal 0.2 weight per cent Na_2O addition did not favorably influence grain refinement and/or retard grain growth after recrystallization. A partial explanation for this phenomenon was the apparently low retention of Na_2O during vacuum sintering as previously described.

Figures 15 through 18 illustrate representative recrystallized microstructures of unalloyed tungsten and the 1, 4, and 8 volume per cent dispersoid alloys of thoria and zirconia, respectively, prepared from aqueous and colloidal additions.

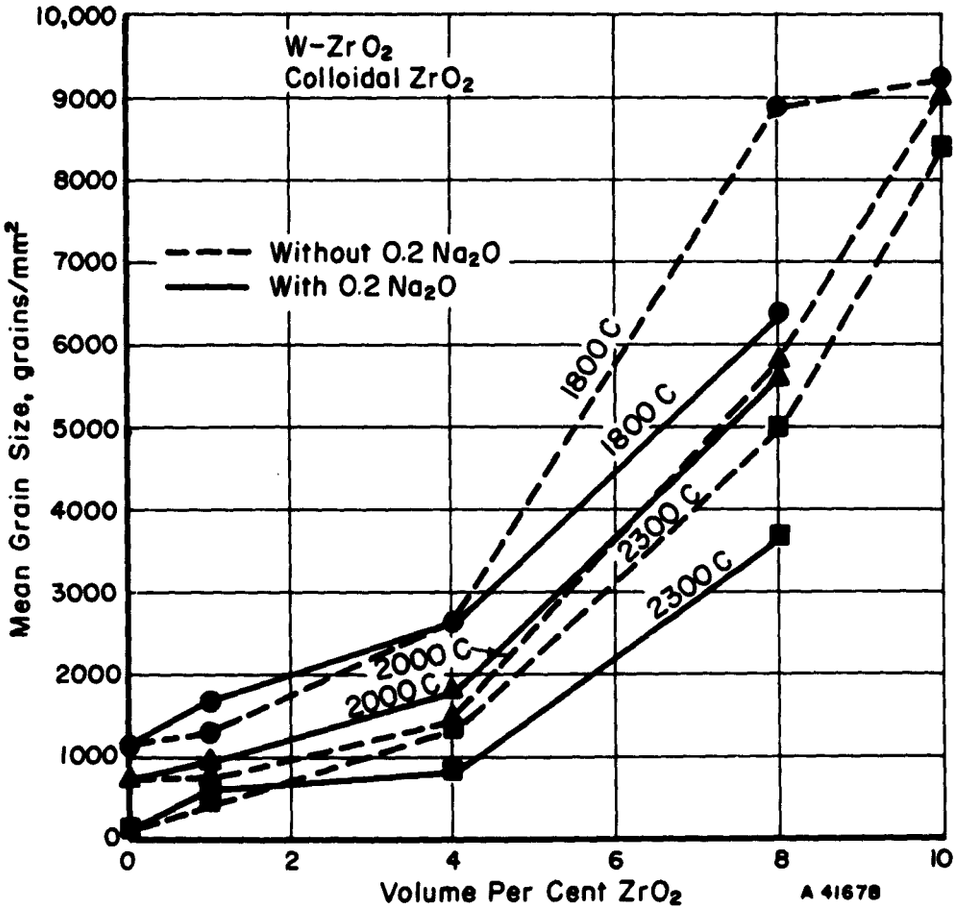


FIGURE 13. EFFECT OF INCREASING ZIRCONIA CONTENT ON THE RECRYSTALLIZED GRAIN SIZE OF THE ZIRCONIA DISPERSOID ALLOYS PREPARED FROM 0.01-MICRON COLLOIDAL ZIRCONIA AND ANNEALED FOR 1 HOUR AT THE INDICATED TEMPERATURES

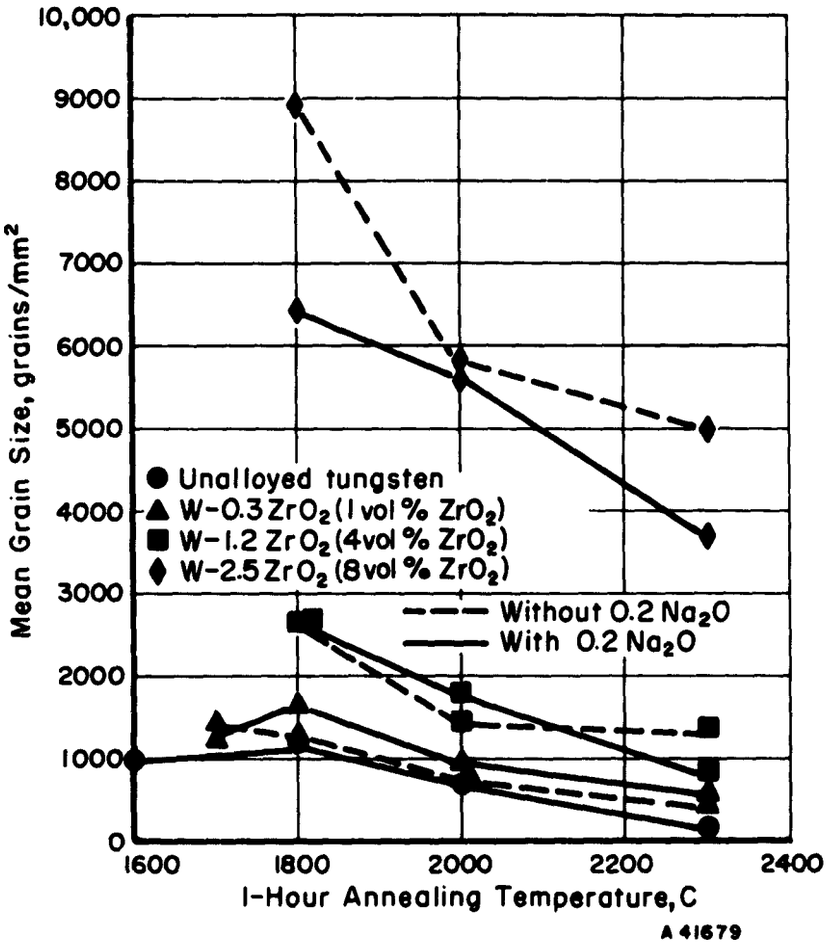


FIGURE 14. GRAIN-GROWTH BEHAVIOR AT UNALLOYED TUNGSTEN AND THE 1, 4, AND 8 VOLUME PER CENT ZIRCONIA DISPERSOID ALLOYS PREPARED FROM 0.01-MICRON COLLOIDAL ZIRCONIA

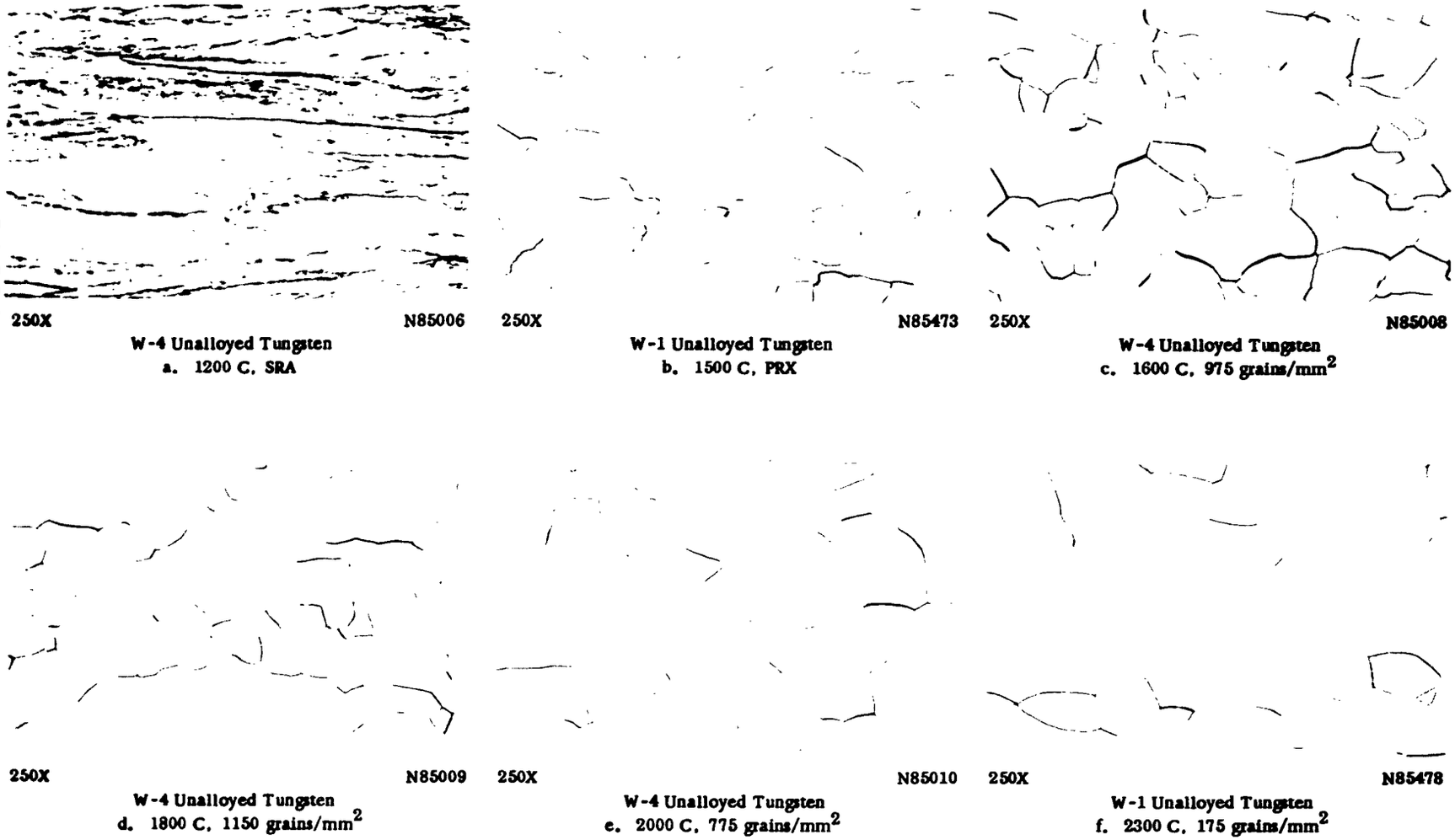
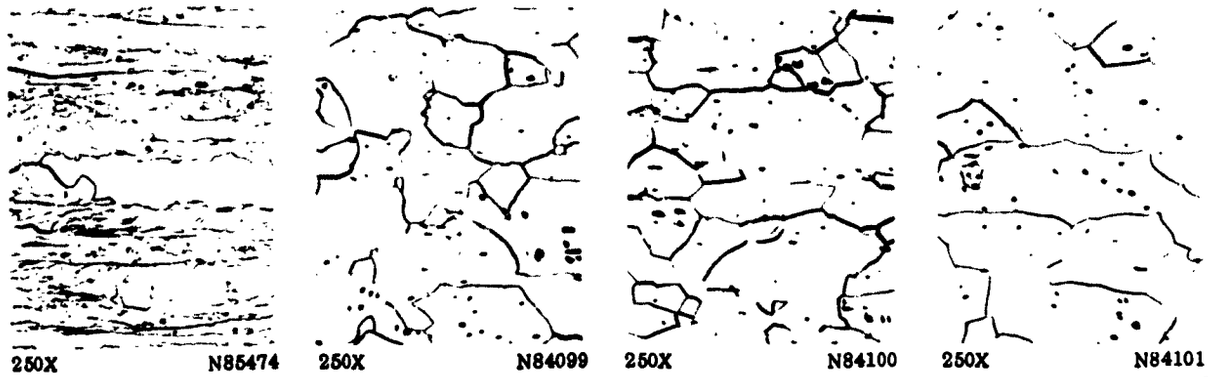


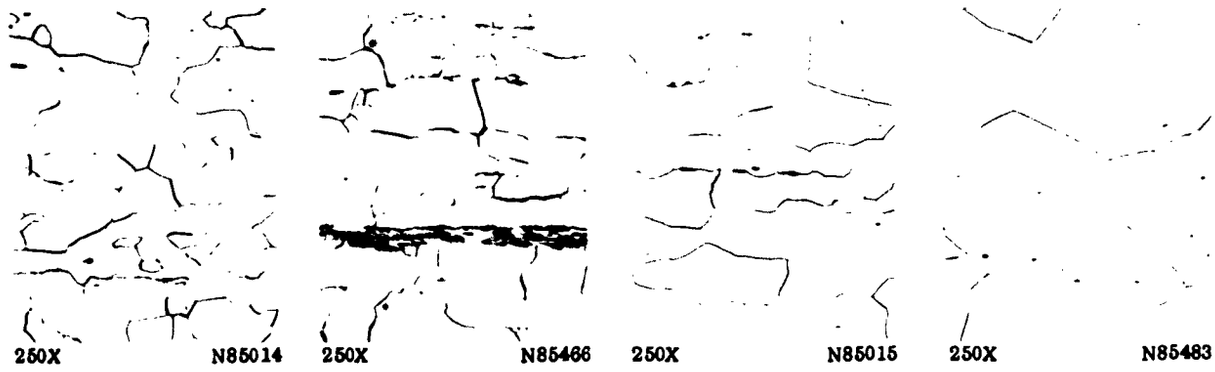
FIGURE 15. LONGITUDINAL MICROSTRUCTURES OF UNALLOYED TUNGSTEN ILLUSTRATING STRUCTURAL CHANGES OCCURRING AFTER ANNEALING 1 HOUR AT THE INDICATED TEMPERATURES

Murakami's etch.



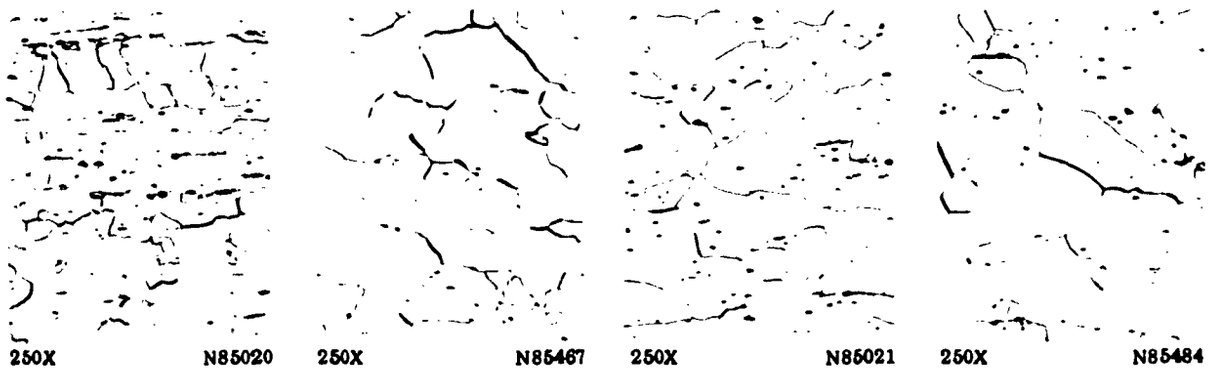
a. 1500 C, PRX b. 1600 C, 1450 grains/mm^2 c. 1800 C, 1425 grains/mm^2 d. 2300 C, 600 grains/mm^2

WD-1, W-0.5ThO_2·0.2Na_2O (1 Volume % ThO_2)



e. 1600 C, PRX f. 1700 C, 1450 grains/mm^2 g. 1800 C, 1300 grains/mm^2 h. 2300 C, 425 grains/mm^2

WD-29, W-0.3ZrO_2 (1 Volume % ZrO_2)

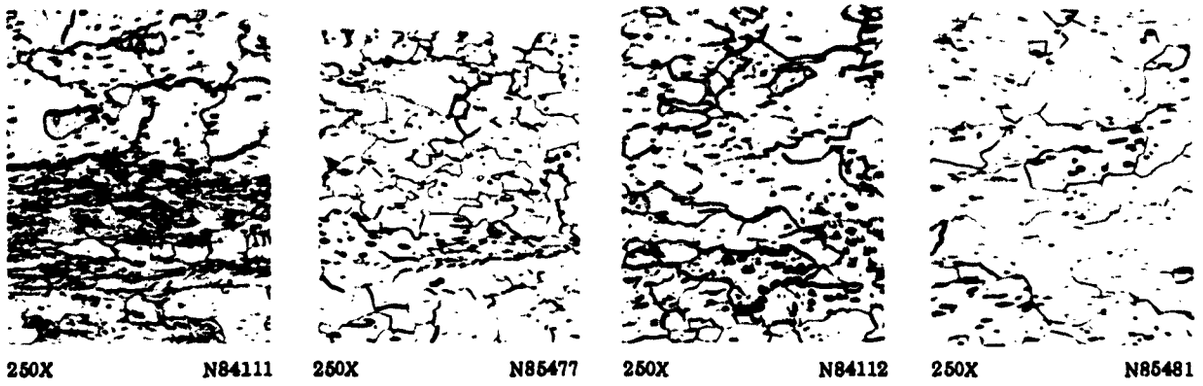


i. 1600 C, PRX j. 1700 C, 1275 grains/mm^2 k. 1800 C, 1675 grains/mm^2 l. 2300 C, 600 grains/mm^2

WD-24, W-0.3ZrO_2·0.2Na_2O (1 Volume % ZrO_2)

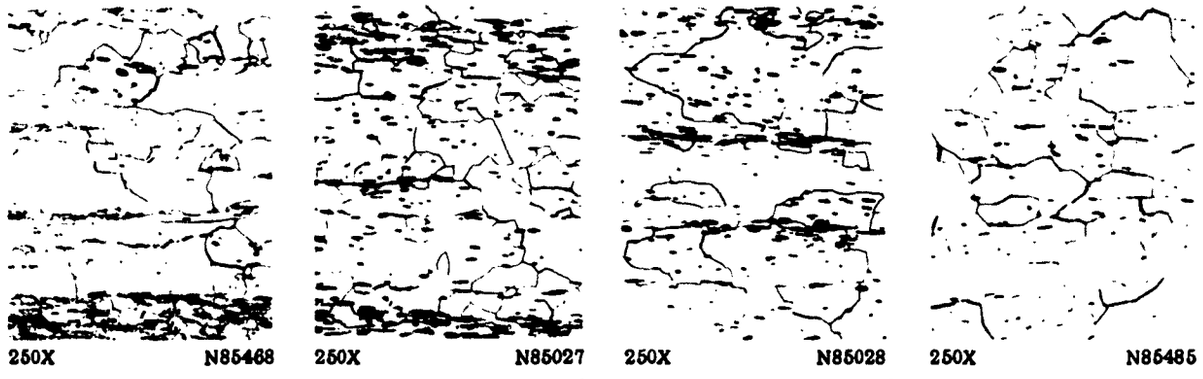
FIGURE 16. LONGITUDINAL MICROSTRUCTURES OF THE 1 VOLUME PER CENT DISPERSOID ALLOYS ILLUSTRATING STRUCTURAL CHANGES OCCURRING AFTER ANNEALING 1 HOUR AT THE INDICATED TEMPERATURES

Murakami's etch.



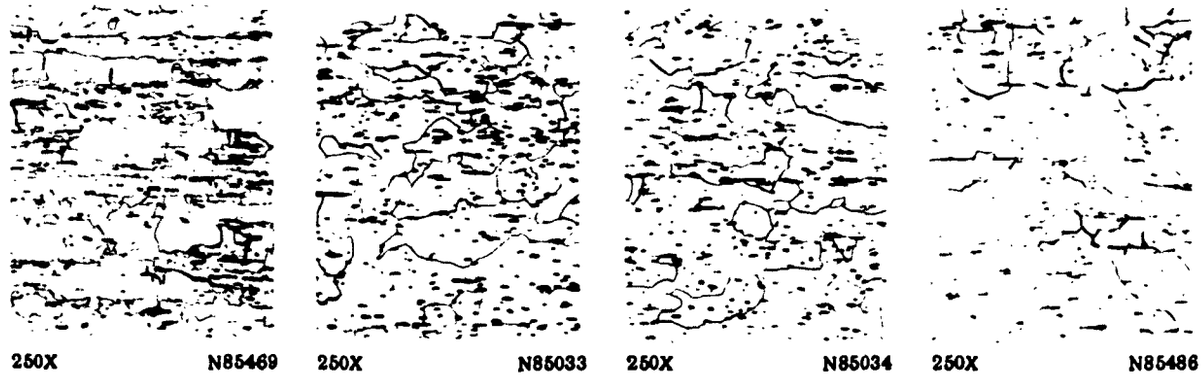
250X N84111 — a. 1600 C, PRX
250X N85477 — b. 1700 C, 2850 grains/mm^2
250X N84112 — c. 1800 C, 2900 grains/mm^2
250X N85481 — d. 2300 C, 900 grains/mm^2

WD-12, W-2.2ThO_2·0.2Na_2O (4 Volume % ThO_2)



250X N85468 — e. 1700 C, PRX
250X N85027 — f. 1800 C, 2650 grains/mm^2
250X N85028 — g. 2000 C, 1450 grains/mm^2
250X N85485 — h. 2300 C, 1375 grains/mm^2

WD-20, W-1.2ZrO_2 (4 Volume % ZrO_2)

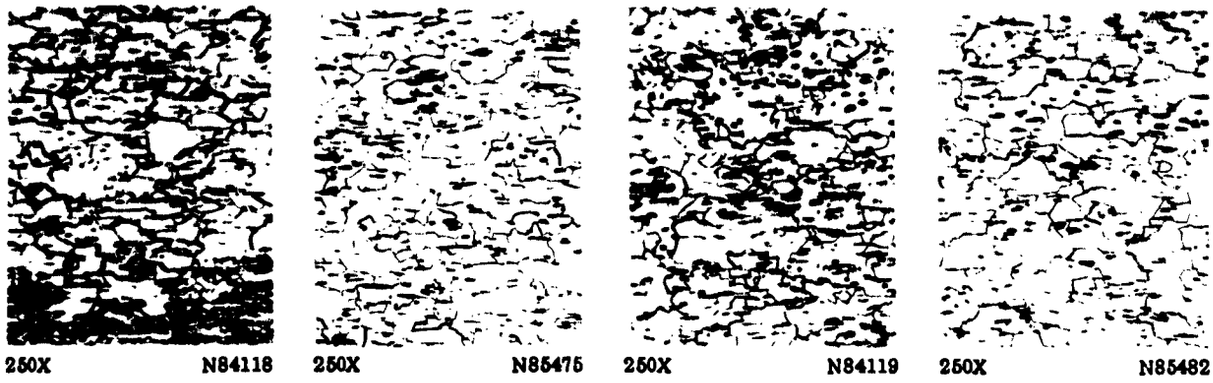


250X N85469 — i. 1700 C, PRX
250X N85033 — j. 1800 C, 2625 grains/mm^2
250X N85034 — k. 2000 C, 1800 grains/mm^2
250X N85486 — l. 2300 C, 875 grains/mm^2

WD-25, W-1.2ZrO_2·0.2Na_2O (4 Volume % ZrO_2)

FIGURE 17. LONGITUDINAL MICROSTRUCTURES OF THE 4 VOLUME PER CENT DISPERSOID ALLOYS ILLUSTRATING STRUCTURAL CHANGES OCCURRING AFTER ANNEALING 1 HOUR AT THE INDICATED TEMPERATURES

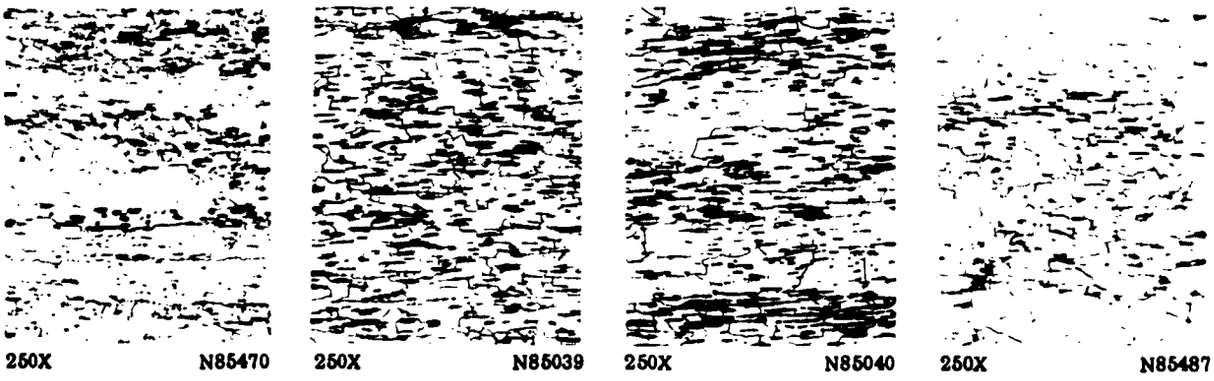
Murakami's etch.



250X N84118 | 250X N85475 | 250X N84119 | 250X N85482

a. 1800 C, PRX | b. 1900 C, 6800 grains/mm^2 | c. 2000 C, 6300 grains/mm^2 | d. 2300 C, 5000 grains/mm^2

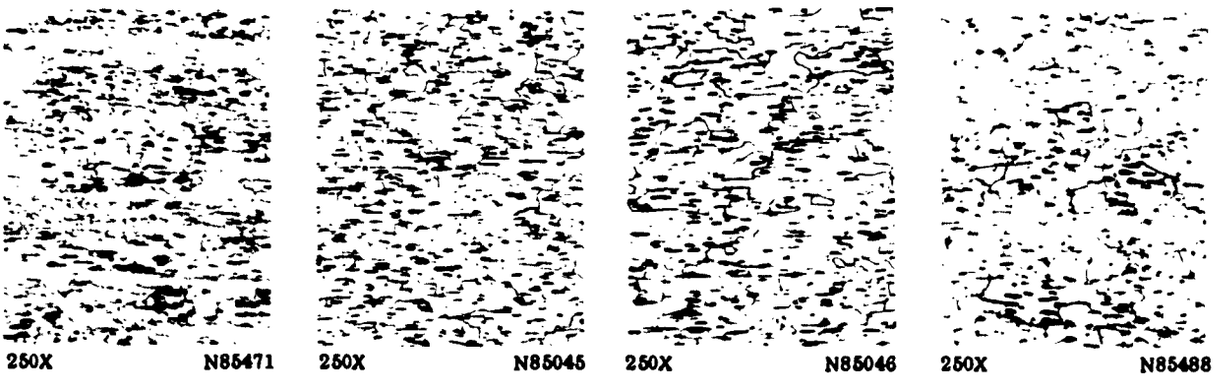
WD-13 W-4.4ThO_2·0.2Na_2O (8 Volume % ThO_2)



250X N85470 | 250X N85039 | 250X N85040 | 250X N85487

e. 1700 C, PRX | f. 1800 C, 8900 grains/mm^2 | g. 2000 C, 5800 grains/mm^2 | h. 2300 C, 5000 grains/mm^2

WD-21 W-2.5ZrO_2 (8 Volume % ZrO_2)



250X N85471 | 250X N85045 | 250X N85046 | 250X N85488

i. 1700 C, PRX | j. 1800 C, 6400 grains/mm^2 | k. 2000 C, 5600 grains/mm^2 | l. 2300 C, 3700 grains/mm^2

WD-26 W-2.5ZrO_2·0.2Na_2O (8 Volume % ZrO_2)

FIGURE 18. LONGITUDINAL MICROSTRUCTURES OF THE 8 VOLUME PER CENT DISPERSOID ALLOYS ILLUSTRATING STRUCTURAL CHANGES OCCURRING AFTER ANNEALING 1 HOUR AT THE INDICATED TEMPERATURES

Murakami's etch.

As shown in Figure 15, unalloyed tungsten was characterized by a minimum 1-hour recrystallization temperature of 1600 C which yielded a completely equiaxed microstructure. Subsequent annealing at higher temperatures of 2000 C and above resulted in significant, preferential grain growth which gave rise to mixed structures consisting of both equiaxed and elongated grains. Grain count decreased from a value of 1150 grains/mm^2 after annealing at 1800 C to 775 and 175 grains/mm^2 (shown in Figures 15e and 15f respectively) after annealing at 2000 C and 2300 C.

The 1, 4, and 8 volume per cent dispersoid alloys shown in Figures 16 through 18 all recrystallized to much smaller grain sizes than did unalloyed tungsten. Also, mixed grain sizes prevailed for all of the 4 and 8 volume per cent alloys from their minimum 1-hour recrystallization temperature through annealing at 2300 C. Only the 1 volume per cent dispersoid alloys shown in Figure 16 displayed tendencies to become equiaxed. However, even at this low level of thoria or zirconia, the recrystallized grains were interlocked to a greater extent than were those of unalloyed tungsten.

The former conclusions that the effects of a 0.2 weight per cent addition of Na_2O were not clearly defined in the group of W-ZrO_2 alloys is also illustrated in Figures 16 through 18. Comparisons between the microstructures both with and without Na_2O at each volume per cent level showed distinct similarity and demonstrated the reversal effects of grain refinement previously discussed.

The resultant thoria and zirconia particle sizes, shapes, and their distributions were also investigated for each of the wrought and recrystallized structures of the dispersoid alloys. Generally, discrete particle sizes varied between 1 and 15 microns and were independent of the dispersoid type, content, or the technique used in preparation. In all of the as-wrought alloys, the dispersed particles were randomly distributed throughout the tungsten matrix and tended to become elongated in the direction of rolling during successive stages of fabrication.

When recrystallized, the inert particles remained randomly dispersed in the 1 volume per cent alloy; however, distinct tendencies for the dispersions to coalesce into stringers or bands were evident with dispersoid contents of 4 volume per cent or greater. Disregarding the coalesced masses of dispersions, the individual particle sizes remained within the range of 1 to 15 microns.

Bend Transition Temperature

Individual bend specimens, each 36 to 39 mils in thickness by 1/4 by 3/4 inch, were cut from the 20 as-wrought dispersoid alloys including unalloyed tungsten. The surfaces of each bend specimen were then ground through 400-grit paper and electropolished using a current density of 6 amp/$in.^2$ in a 2 per cent sodium hydroxide solution. Smooth bright surfaces resulted.

A sample was tested at a given temperature by bridging it across a 75-degree female V-die and successively bending it through an included angle of 105 degrees with male dies of progressively smaller radii until cracking or complete fracture occurred. Seven or eight specimens were tested for unalloyed tungsten and each alloy at temperatures throughout the ductile-to-brittle transition range, thus defining the transition temperature for a given material.

For comparative purposes, bend ductility was conveniently defined in terms of a T-value, where T represents the ratio of the smallest successful bend-die radius to the sheet thickness. With this parameter as a measure of ductility, 0T represents excellent ductility, while T-values of 12 or greater represent a brittle condition. In most cases, the transition from brittle to ductile behavior occurred over a fairly small temperature interval. For convenience in comparisons, the lowest temperature at which the bend ductility of a given material was decreased to a given T-value was defined as the transition temperature of that material.

Table 9 summarizes the results of 62 bend-transition temperature determinations on the 20 dispersoid alloys annealed for 1 hour at temperatures ranging from 1000 C to 2300 C. In this table 4T transition temperatures as well as 8T values are tabulated.

Separate discussions of the ductile-to-brittle bend-transition temperature testing conducted on unalloyed tungsten and the three groups of dispersoid alloys are presented as follows.

Unalloyed Tungsten

Figure 19 shows the individual transition-temperature curves for unalloyed tungsten after annealing for 1 hour at 1000 C, 1200 C, 1300 C, 1400 C, 1800 C, 2000 C, and 2300 C. The first three temperatures of 1000 C, 1200 C, and 1300 C were stress-relief annealing conditions which preserved the fiberous microstructures typical of as-wrought material. However, annealing at 1400 C effected partial recrystallization, while temperatures of 1800 C, 2000 C, and 2300 C promoted complete recrystallization and grain growth.

Variations of the transition temperature with annealing conditions are obvious from reviewing Figure 15. A slight reduction of the transition temperature from 210 C to 200 C was obtained by stress relieving for 1 hour at either 1200 C or 1300 C rather than at 1000 C. This result is significant and is consistent with the information currently being reported by the Fansteel Metallurgical Corporation in their work on The Tungsten Sheet Rolling Program for the Navy. (1)

Annealing at 1400 C resulted in a significant 110-degrees increase in the transition temperature to 310 C which reflected the partially recrystallized condition of this material.

Further testing of unalloyed tungsten annealed for 1 hour at 1800 C, 2000 C, and 2300 C resulted in completely recrystallized material with respective grain sizes of 1175, 725, and 175 grains/mm^2. Associated with the progressively increasing grain sizes were progressively increasing transition temperatures of 350 C, 375 C, and 390 C, thereby again demonstrating the well-known dependency of transition temperature on grain size.

Tungsten-Thoria Alloys

Figure 20 summarizes the effect of increasing thoria content on transition temperature after annealing for 1 hour at 1000 C, 1200 C, and 1800 C. Generally, the tendency shown in this figure was for transition temperature to decrease continuously with increasing thoria content for a given annealing condition. Both 1000 C and 1200 C were

TABLE 9. SUMMARY OF DUCTILE-TO-BRITTLE BEND TRANSITION TEMPERATURES AND GRAIN-STRUCTURE PARAMETERS FOR UNALLOYED TUNGSTEN AND THE DISPERSOID ALLOYS

Alloy	Nominal Alloy Content		Approximate 1-Hr Recrystallization Temperature, C	1-Hr Annealing Temperature, C	N_A, Mean Grain Size[a], grains/mm^2	S_v, Mean[c] Grain-Boundary Surface Area, $\frac{mm^2}{mm^3}$	8T Transition Temperature		4T Transition Temperature	
	Weight Per Cent	Volume Per Cent					C	F	C	F
				Unalloyed Tungsten						
W-2	100W	100W	1600	1000	SRW	--	210	410	210	410
				1200	SRW	--	200	392	200	392
				1300	SRW	--	200	392	210	410
				1400	PRX	--	310	590	320	608
				1800	1175	81.3	350	622	350	662
				2000	775	60.6	375	707	460	860
				2300	175	31.4	390	734	450	842
W-4	100W	100W	1600	1000	SRW	--	210	410	210	410
W-3[b]	100W	100W	1600	1200	SRW	--	175	347		
				Thoria Dispersoid Alloys Prepared From Aqueous Additions						
WD-1	0.5ThO_2·0.2Na_2O	1ThO_2	1600	1000	SRW	--	175	347	175	347
				1200	SRW	--	225	437	225	437
				1800	1425	88.9	350	662	365	688
WD-11	1.1ThO_2·0.2Na_2O	2ThO_2	1700	1000	SRW	--	175	347	175	347
				1200	SRW	--	185	365	185	365
				1800	2125	109	325	617	350	662
WD-12	2.2ThO_2·0.2Na_2O	4ThO_2	1700	1000	SRW	--	140	284	140	284
				1200	SRW	--	150	302	150	302
				1800	2900	129	300	572	330	626
WD-13	4.4ThO_2·0.2Na_2O	8ThO_2	1900	1000	SRW	--	150	302	160	320
				1200	SRW	--	110	230	135	275
				1300	SRW	--	85	185	115	239
				1400	SRW	--	95	203	135	275
				1800	PRX	--	275	527	290	554
				2000	6300	187	300	572	325	617
				2300	5000	167	335	635	350	662
				Zirconia Dispersoid Alloys From Aqueous Additions						
WD-9	0.3ZrO_2·0.2Na_2O	1ZrO_2	1800	1000	SRW	--	165	329	170	338
				1200	SRW	--	175	347	180	356
WD-14	1.2ZrO_2	4ZrO_2	1800	1000	SRW	--	130	266	130	266
				1200	SRW	--	205	401	205	401
WD-28	1.2ZrO_2·0.2Na_2O	4ZrO_2	1800	1000	SRW	--	185	365	185	365
				1200	SRW	--	200	392	200	392
WD-7	2.5ZrO_2	8ZrO_2	1800	1000	SRW	--	200	392	200	392
				1200	SRW	--	235	455	235	455
WD-10	2.5ZrO_2·0.2Na_2O	8ZrO_2	1800	1000	SRW	--	175	347	195	383
				1200	SRW	--	175	347	200	392
WD-18	3.1ZrO_2	10ZrO_2	1800	1000	SRW	--	130	266	150	302
				1200	SRW	--	165	329	180	356

TABLE 9. (Continued)

Alloy	Nominal Alloy Content, Weight Per Cent	Nominal Alloy Content, Volume Per Cent	Approximate 1-Hr Recrystallization Temperature,	1-Hr Annealing Temperature, C	N_A, Mean Grain Size[a], grains/mm^2	S_V, Mean[c] Grain-Boundary Surface Area, $\frac{mm^2}{mm^3}$	8T Transition Temperature, C	8T Transition Temperature, F	4T Transition Temperature, C	4T Transition Temperature, F
				Zirconia Dispersoid Alloys Prepared From 0.01-Micron Colloidal Zirconia						
WD-29	$0.3ZrO_2$	$1ZrO_2$	1700	1000	SRW	--	160	320	160	320
				1200	SRW	--	165	329	200	392
				1800	1300	86.0	360	680	400	752
WD-24	$0.3ZrO_2 \cdot 0.2Na_2O$	$1ZrO_2$	1700	1000	SRW	--	175	347	175	347
				1200	SRW	--	190	374	190	374
				1800	1675	97.4	340	644	395	743
WD-20	$1.2ZrO_2$	$4ZrO_2$	1800	1000	SRW	--	175	347	175	347
				1200	SRW	--	175	347	200	392
				1800	2650	124	325	617	355	671
WD-25	$1.2ZrO_2 \cdot 0.2Na_2O$	$4ZrO_2$	1800	1000	SRW	--	185	365	185	365
				1200	SRW	--	165	329	170	338
				1800	2625	122	300	572	345	653
WD-21	$2.5ZrO_2$	$8ZrO_2$	1800	1000	SRW	--	140	284	185	365
				1200	SRW	--	150	302	210	410
				1800	8900	224	260	500	315	599
WD-26	$2.5ZrO_2 \cdot 0.2Na_2O$	$8ZrO_2$	1800	1000	SRW	--	140	284	140	284
				1200	SRW	--	115	239	145	293
				1300	SRW	--	90	194	90	194
				1400	SRW	--	175	347	175	347
				1800	6400	188	260	500	290	554
				2000	5600	197	300	572	345	653
				2300	3700	144	350	662	450	842
WD-22	$3.1ZrO_2$	$10ZrO_2$	1800	1000	SRW	--	140	284	155	311
				1200	SRW	--	125	257	170	338
				1800	9250	232	<250	<464	280	536

(a) SRW - Stress-relieved wrought material
PRX - Partially recrystallized material.
(b) Vacuum-radiation sintered for 4 hours at 2300 C.
(c) $S_V = 2N_L$; where N_L = grains/mm determined from line-intercept counting.

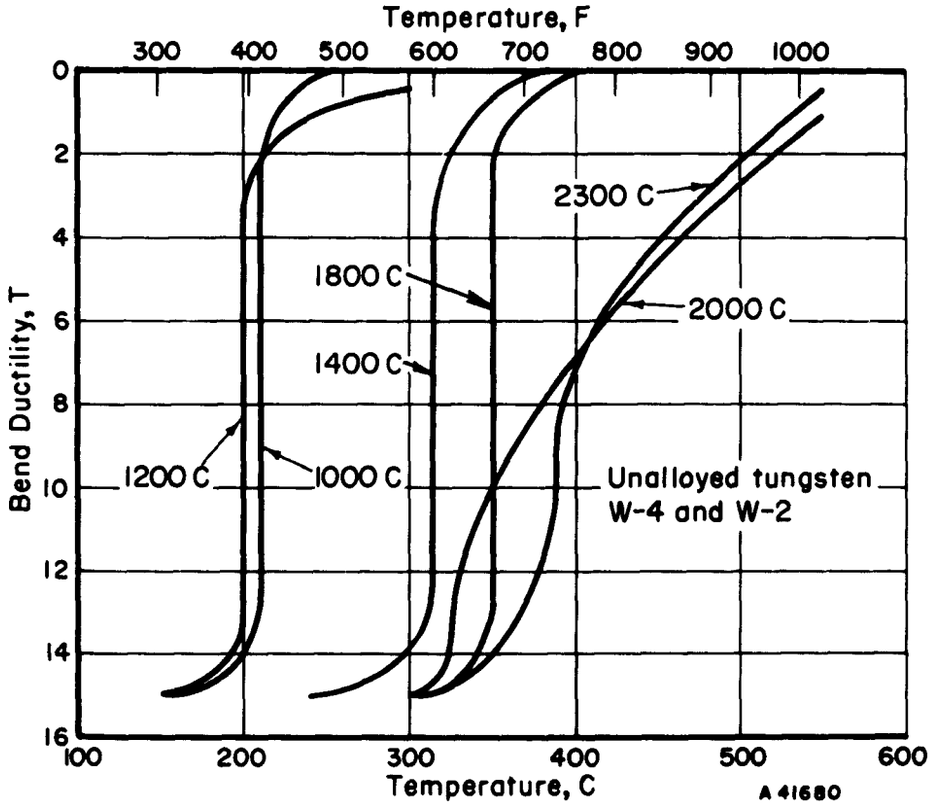


FIGURE 19. DUCTILE-TO-BRITTLE TRANSITION CHARACTERISTICS OF WROUGHT UNALLOYED TUNGSTEN ANNEALED FOR 1 HOUR AT THE INDICATED TEMPERATURES

stress-relieving conditions, while 1800 C effected complete recrystallization in all of the alloys except the 8 volume per cent composition which was only partially recrystallized.

The most significant feature of the transition-temperature data represented in Figure 20 is the comparison between the two curves representing the stress-relief annealing conditions. At thoria levels below 4.5 volume per cent except for unalloyed tungsten, annealing at 1000 C was preferred, as consistently lower transition temperatures resulted. However, with thoria levels greater than 4.5 volume per cent, annealing at 1200 C rather than 1000 C resulted in a significant decrease in transition temperature. The most pronounced example of this was shown by the 8 volume per cent thoria alloy for which the transition temperature was decreased from 150 C to 110 C. Annealing treatments at 1300 C and 1400 C on the 8 volume per cent alloy resulted in respective transition temperatures of 85 C and 90 C. These were both the lowest values obtained for the 8 volume per cent composition and the entire group of W-ThO_2 alloys.

After annealing at 1800 C, the lowest transition temperature (275 C) was also associated with the 8 volume per cent composition. From the 1800 C curve shown in Figure 20, it is significant to note that the progressively lower transition temperatures associated with increasing thoria content also correlated with grain size. In each instance, the lower transition temperatures resulted with the finer recrystallized grain sizes. This not only points out the effect of grain size on transition temperature but also suggests the importance of thoria additions as grain-refining agents to achieve lower transition temperatures.

Tungsten-Zirconia Alloys

Figures 21 and 22 summarize the effect of increasing zirconia content on transition temperature after annealing for 1 hour at the indicated temperatures. Generally, the tendency shown in these figures was for transition temperature to decrease continuously with increasing zirconia content for a given annealing condition.

Figure 21 shows the influence of zirconia content on the transition temperatures of stress-relieved W-ZrO_2 alloys prepared from aqueous additions. As compared with those for the W-ThO_2 series, the curves shown in Figure 21 were highly erratic. However, for each class of alloys, i.e., with and without 0.2Na_2O, and for both annealing conditions, the general tendency was toward lower transition temperatures with increasing zirconia content. Comparisons made between the 1-hour stress-relieving conditions of 1000 C and 1200 C for each class of materials showed 1000 C rather than 1200 C to be preferred since, except for unalloyed tungsten, the former yielded lower transition temperatures.

Erratic behavior of fabricability, grain sizes, and transition temperatures was characteristic of the W-ZrO_2 alloys prepared from aqueous additions. Therefore, on the basis of these collective observations, the entire group of aqueously prepared materials was dropped from further experimental consideration in this program.

Figure 22 shows the collective bend transition characteristics of the W-ZrO_2 alloys prepared from colloidal zirconia. Each alloy, both with and without 0.2Na_2O, was annealed for 1 hour at 1000 C, 1200 C, and 1800 C. Both 1000 C and 1200 C was stress-relief-annealing conditions, while 1800 C accomplished complete recrystallization in all of the alloys. Generally, the tendency shown in Figure 22 was for transition temperature to decrease with increasing zirconia content.

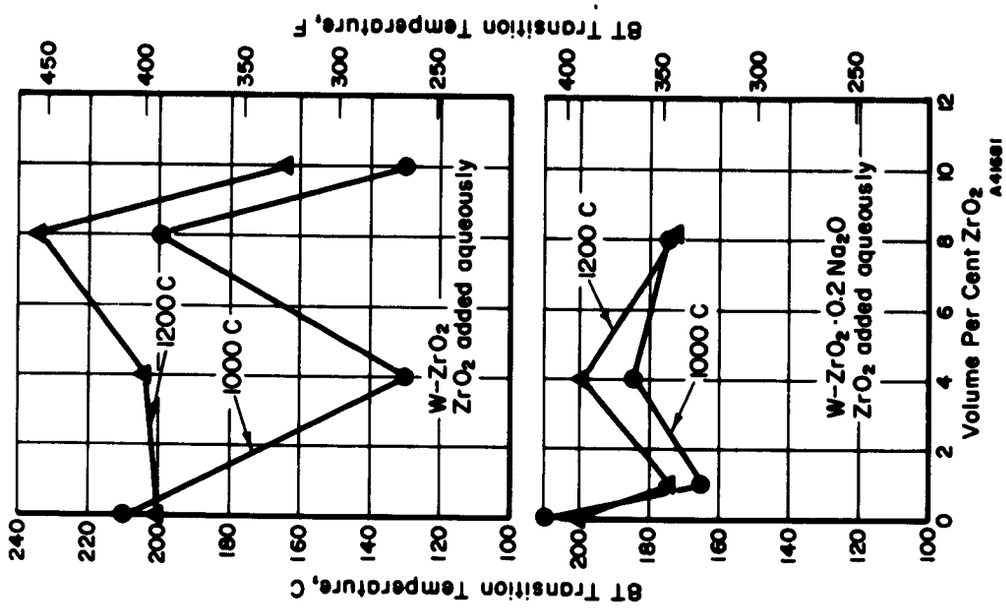


FIGURE 21. EFFECT OF INCREASING ZIRCONIA CONTENT WITH AND WITHOUT 0.2 WEIGHT PER CENT Na_2O ON THE TEMPERATURES OF DUCTILE-TO-BRITTLE TRANSITION IN THE W-ZrO_2 ALLOY SERIES PREPARED FROM AQUEOUS ADDITIONS AND ANNEALED FOR 1 HOUR AT THE INDICATED TEMPERATURES

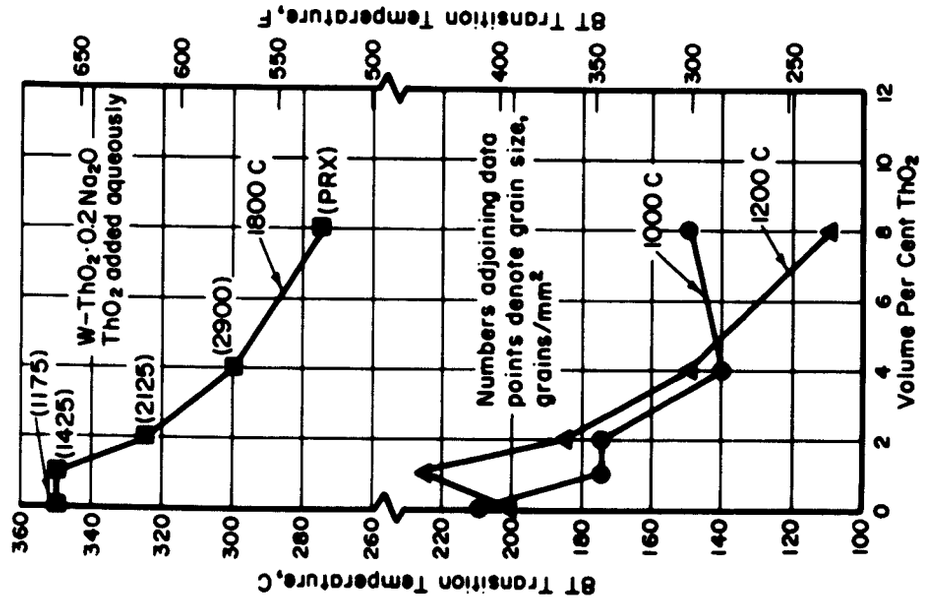


FIGURE 20. EFFECT OF INCREASING THORIA CONTENT ON THE TEMPERATURES OF DUCTILE-TO-BRITTLE BEND TRANSITION IN THE W-ThO_2·0.2Na_2O ALLOY SERIES PREPARED FROM AQUEOUS ADDITIONS AND ANNEALED FOR 1 HOUR AT THE INDICATED TEMPERATURES

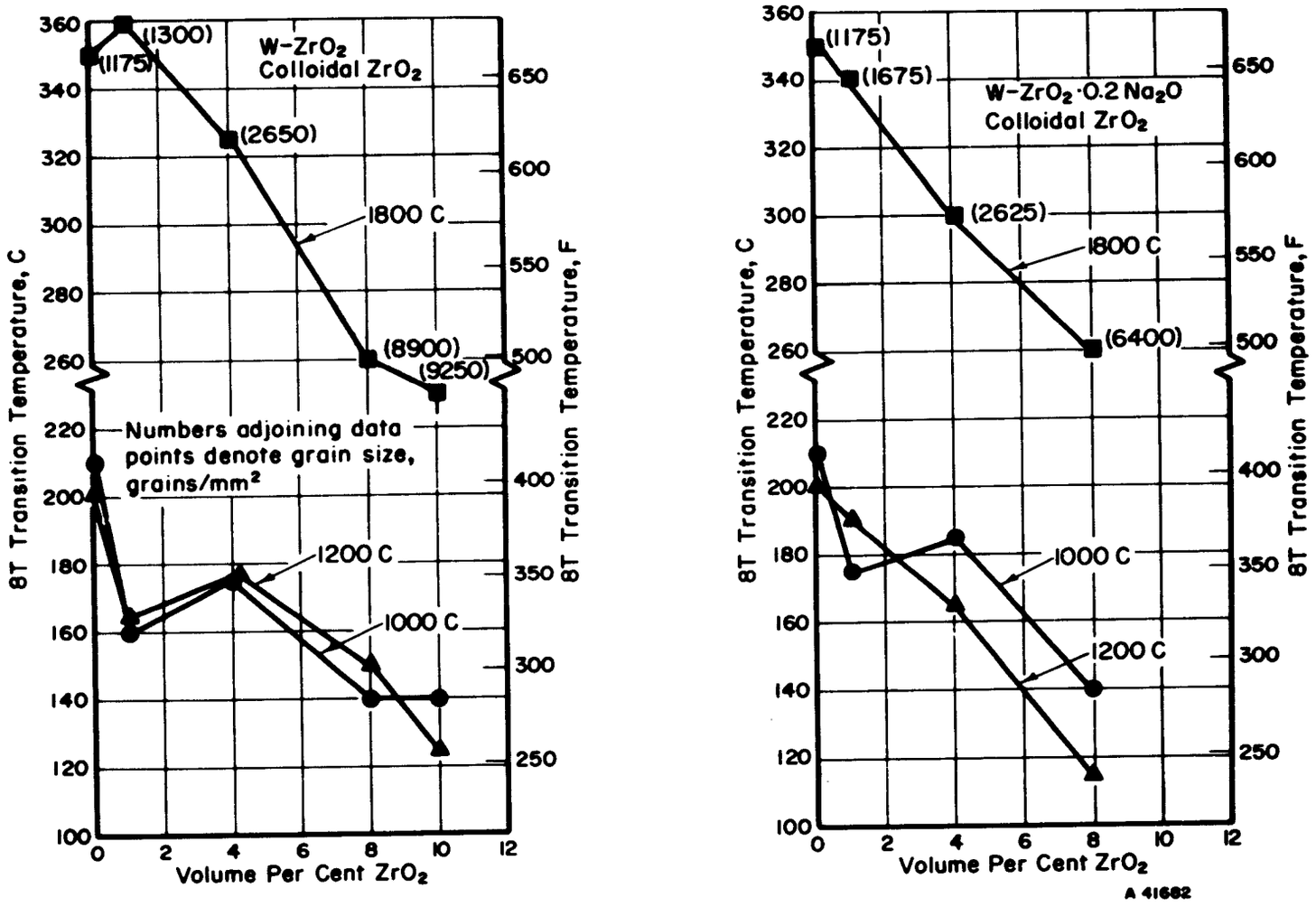


FIGURE 22. EFFECT OF INCREASING ZIRCONIA CONTENT WITH AND WITHOUT 0.2 WEIGHT PER CENT Na_2O ON THE TEMPERATURES OF DUCTILE-TO-BRITTLE BEND TRANSITION IN THE $W-ZrO_2$ ALLOY SERIES PREPARED FROM 0.01-MICRON COLLOIDAL ZIRCONIA AND ANNEALED FOR 1 HOUR AT THE INDICATED TEMPERATURES

For those alloys without Na_2O, stress-relief annealing at 1000 C rather than 1200 C resulted in slightly lower transition temperatures through approximately 9 volume per cent zirconia.

Except for the 1 volume per cent alloy, the transition temperatures of each alloy containing Na_2O showed a greater decrease on increasing the stress-relieving temperature from 1000 C to 1200 C. The most pronounced examples of this were shown by the 4 and 8 volume per cent alloys for which the transition temperature decreased 20 and 25 degrees, respectively. Increasing annealing temperatures for the 8 volume per cent zirconia alloy containing Na_2O to 1300 C and 1400 C resulted in respective transition temperatures of 90 C and 175 C. The value of 90 C was the minimum value obtained for both the 8 volume per cent composition and the entire group of W-ZrO_2 alloys.

The variation of transition temperatures in the colloidal W-ZrO_2 group after annealing at 1800 C showed a similar dependency on both alloy content and grain size to that previously noted for the W-ThO_2 group. Each class of alloys, i.e., with and without Na_2O, tended toward lower transition temperatures and progressively finer grain sizes with increasing zirconia content. The lowest transition temperature of practical value obtained was 260 C. This was characteristic of the 8 volume per cent alloys both with and without Na_2O having respective grain sizes of 6400 and 8900 grains/mm^2.

Figure 23 illustrates the effect of increasing 1-hour annealing temperature on the transition temperatures of unalloyed tungsten and both 8 volume per cent alloys of thoria and zirconia containing 0.2Na_2O. As previously discussed, these two dispersoid alloys produced the lowest transition temperatures within their respective series and are represented here for purposes of comparison.

The significant feature of Figure 23 is the proximity of the curves representing the 8 volume per cent alloys and their position relative to that shown for unalloyed tungsten. Reductions in the transition temperatures ranging from 40 to 215 degrees occurred over the range of annealing temperatures in favor of the dispersoid alloys as compared with unalloyed tungsten. In conjunction with this, similar transition temperatures were obtained at each annealing temperature for both dispersoid alloys. This suggests that the transition temperatures of these alloys are dependent more on the level of dispersoid content present than on the type, i.e., thoria or zirconia. However, with the recrystallized structures annealed at 1800 C and higher, grain size is also an important factor. Generally, the ductile-to-brittle transition temperatures increased with increasing recrystallized grain size. This effect was consistently observed for the recrystallized data shown in Figure 23 and suggested that a correlation between grain size and transition temperature might exist irrespective of dispersoid content.

Figure 24 illustrates the attempt to relate the transition temperatures of all the recrystallized tungsten-base materials to grain size. The results were significant and resolved the dispersoid alloys into two categories with respect to the effect of grain size on transition temperature. The grain-size parameter selected for this correlation was the mean grain-boundary surface area, S_v, for each recrystallized structure. As defined in the footnote to Table 9, $S_v = 2N_L$, where N_L is the mean number of grains per millimeter determined from line-intercept counting.

The first category of data, labeled A in Figure 24, illustrated the grain-size effect on transition temperature for unalloyed tungsten and the alloys containing either thoria or

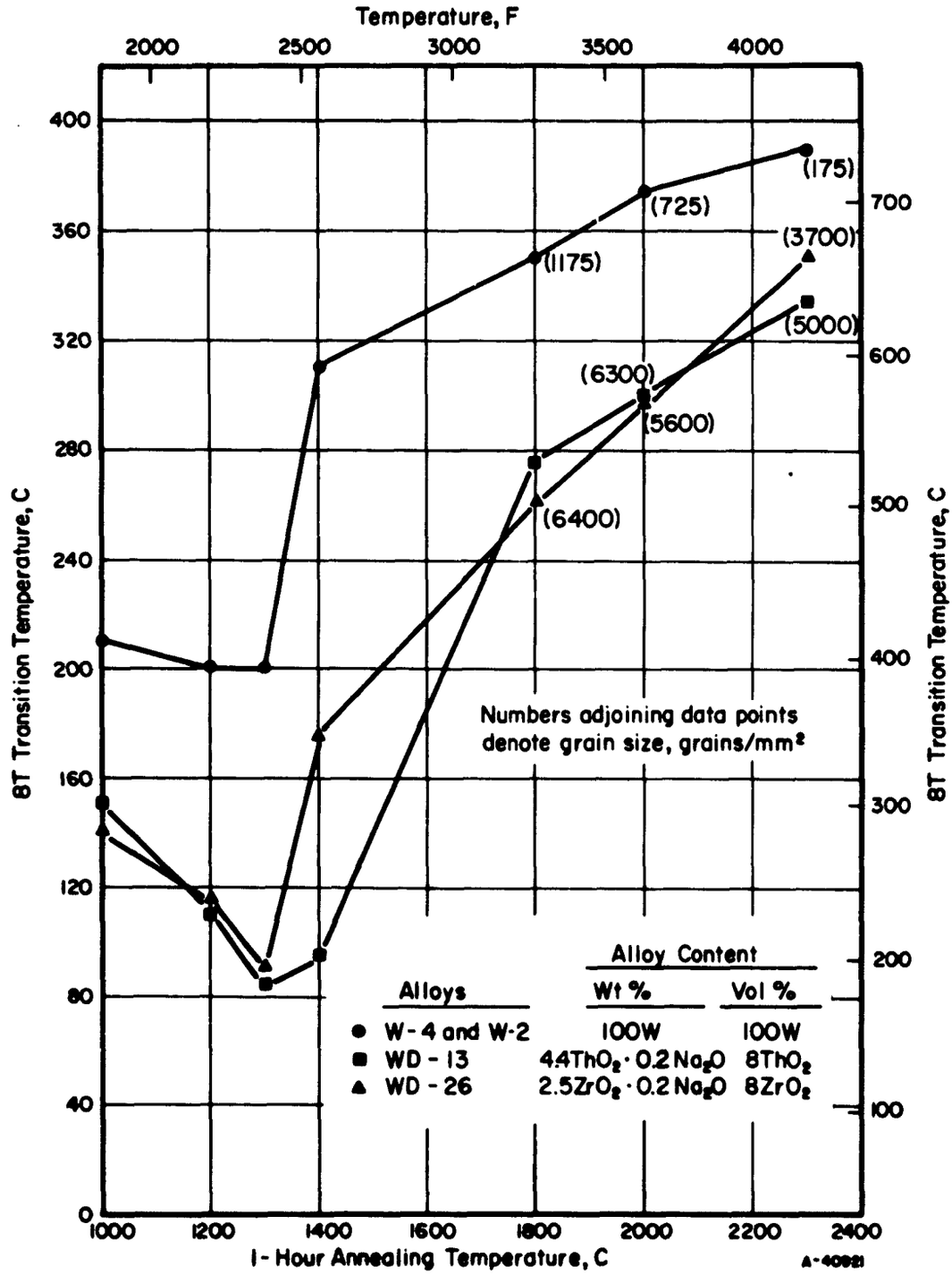


FIGURE 23. EFFECT OF 1-HOUR ANNEALING TEMPERATURES ON THE TEMPERATURES OF DUCTILE-TO-BRITTLE BEND TRANSITION FOR UNALLOYED TUNGSTEN AND THE 8 VOLUME PER CENT DISPERSOID ALLOYS OF THORIA AND ZIRCONIA WITH 0.2 WEIGHT PER CENT Na_2O

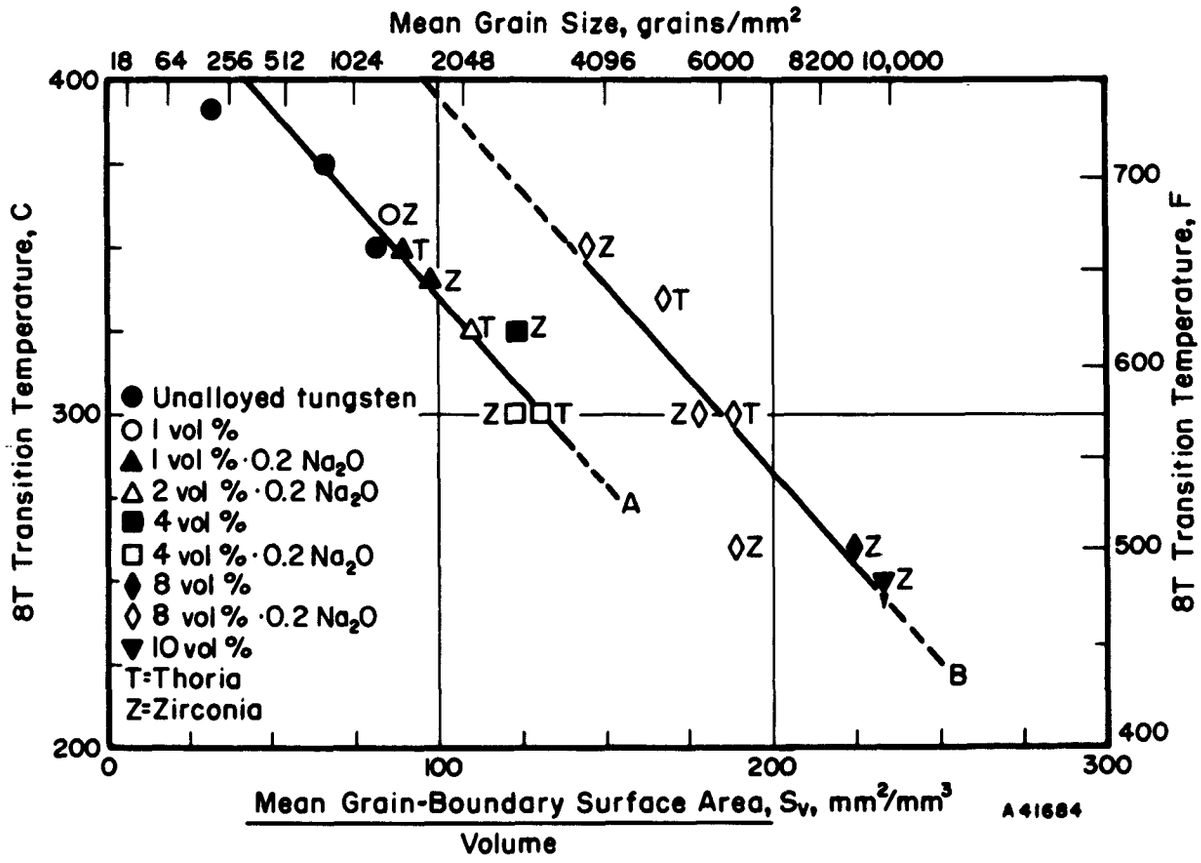


FIGURE 24. RELATIONSHIP OF THE DUCTILE-TO-BRITTLE TRANSITION TEMPERATURES TO THE MEAN GRAIN-BOUNDARY SURFACE AREAS OF UNALLOYED TUNGSTEN AND ALL OF THE TUNGSTEN-BASE DISPERSOID ALLOYS TESTED

zirconia additions through 4 volume per cent. With progressively increasing grain-boundary surface area, i.e., decreasing grain size, the transition temperatures were observed to decrease. A close observation of the data points which fall along Line A shows that the coarse-grained unalloyed tungsten resulted in the highest transition temperature, 390 C. The data points representing progressive increases in dispersoid content through 4 volume per cent were scattered on down along Line A through lower temperatures to 300 C which was the lowest transition temperature within this category. Summarizing, decreasing transition temperatures were associated with increasing grain-boundary surface area, which in turn was directly related to the level of dispersoid content. From this it was concluded that the transition temperatures were more dependent on the grain-refining effects previously noted for thoria and zirconia than on the dispersoid content per se.

The second category of data, i.e., the points falling along Line B in Figure 24, included the 8 through 10 volume per cent alloys and illustrated the same grain-size effects on transition temperature. The significant feature of Line B was its position relative to Line A. Both were parallel; however, the transition temperatures associated with the 8 to 10 volume per cent alloys were approximately 60 C higher for a given value of grain-boundary surface area than for the alloys of lower dispersoid content. This phenomenon suggested that a grain-boundary embrittling effect might be occurring at dispersoid concentrations above 4 volume per cent. Verification of this was investigated using light-microscopy techniques to examine fractured surfaces of each alloy, both perpendicular and parallel to the plane of fracture. However, due to the fine grain sizes of the alloys containing greater than 4 volume per cent dispersoids and the limitations with light microscopy, no firm conclusions could be drawn regarding the presence of an embrittling phase. The only sound conclusion possible from these studies was that dispersoid content did influence the mode of fracture, i.e., transgranular or intergranular. Recrystallized unalloyed tungsten fractured both transgranularly and intergranularly in an approximately equal proportion, while only slight traces of transgranular fracture was noticed in the 1 volume per cent alloys. For dispersoid contents greater than 1 volume per cent fracture was entirely intergranular.

Tensile Properties

Tensile tests were conducted on unalloyed tungsten and both 8 volume per cent compositions of thoria and zirconia containing 0.2 weight per cent Na_2O. Selection of the two dispersoid alloys for these tests was based on the superior ductility that they had previously displayed during bend testing.

Each material was tested in its optimized stress-relieved condition, i.e., the time-temperature parameters which resulted in the lowest bend transition temperature for the material. For unalloyed tungsten and both 8 volume per cent dispersoid alloys the optimum treatments were 1-hour anneals at 1200 C and 1300 C, respectively.

After proper stress relieving, the bulk of the strip material from each composition was cut into blanks. Preparation of the sheet tensile specimens from these blanks was then accomplished by a combination of grinding and ultrasonic drilling operations. The surfaces, edges, and reduced sections of each specimen were first ground to their respective dimensions, while ultrasonic drilling was used to provide a hole in the shoulders for a pin support. The finished dimensions of a typical specimen were as follows:

(1) 30-mil sheet thickness
(2) 0.125-inch-wide reduced section
(3) 0.750-inch uniform gage length
(4) 0.375-inch shoulder width containing 0.125-inch-diameter pinholes
(5) 3.50 inches over-all length.

Prior to testing, each specimen was electropolished in a 2 per cent NaOH solution. This served the dual purpose of eliminating sharp edges and revealing the presence of any gross imperfections in the material.

Excellent quality unalloyed tungsten specimens were obtained by using these preparation techniques. However, as revealed by electropolishing, both of the 8 volume per cent dispersoid alloys were severely laminated. The laminations were apparently generated in grinding since none were observed in the bend specimens or the as-wrought sheet material. Also, considerable chipping occurred around the edges of the pinholes in the shoulders, thereby weakening these regions.

Fourteen tests were carried out over a temperature range from 38 C to 275 C using an Instron testing instrument. Crosshead speeds of 0.002 inch per minute and 0.02 inch per minute were used while loading each specimen to its yield point and from yield to failure, respectively. During testing, the load elongation behavior of each specimen was automatically recorded. The resultant strengths and ductilities obtained for each material are recorded in Table 10.

Reliable yield-strength values were obtained only for unalloyed tungsten. The yield-strength values obtained for both of the 8 volume per cent dispersoid alloys were questionable, due to the extensive deformation which occurred around the pinholes in the shoulders of these samples.

As shown in Figure 25, the 8 volume per cent zirconia alloy exhibited the maximum ultimate strengths, ranging from 203,500 psi to 164,000 psi over the temperature range from 38 C to 175 C. These strengths were closely paralleled by those of the 8 volume per cent thoria alloy which was tested over a temperature range from 38 C to 275 C. In comparison with the dispersoid alloys, the ultimate strengths of the unalloyed tungsten was consistently lower, decreasing from about 160,000 psi at 125 C to 104,000 psi at 275 C. Also, the comparative slopes of the curves for the dispersoid alloys and unalloyed tungsten show that the former retain superior strengths with increasing test temperatures.

Figure 26 demonstrates the influence of temperature on the tensile ductility of unalloyed tungsten. As stress-relief annealed, this material showed moderately high ductility (better than 17 per cent elongation and 40 per cent reduction in area) at 200 C or greater. Although the ductility values dropped sharply while decreasing the temperature from 275 C to 125 C, the unalloyed sheet still showed appreciable ductility (4 per cent elongation and 12 per cent reduction in area) at the lower temperature. This degree of ductility at 125 C in tension was unexpected in view of the fact that this same material was quite brittle in bending at temperatures below 200 C (see Figure 19). With equivalent strain rates, one would normally expect the ductile-to-brittle transition to occur at higher temperatures when testing in uniaxial tension than when testing in bending which imposes biaxial and possibly triaxial stresses.[3] The apparently reversed situation obtained here for unalloyed tungsten may partly be explained by the fact that the bend tests were carried out using appreciably greater strain rates.

TABLE 10. SUMMARY OF STRENGTH AND DUCTILITY PROPERTIES OBTAINED FOR UNALLOYED TUNGSTEN AND THE 8 VOLUME PER CENT DISPERSOID ALLOYS OF THORIA AND ZIRCONIA

Alloy	Test Temperature, C	Yield Strength, 1000 psi	Ultimate Tensile Strength, 1000 psi	Reduction, in Area[a], per cent	Elongation[a], per cent
		Unalloyed Tungsten[b]			
W-1	125	140.1	161.0	12.0	4.0
W-4	175	109.7	126.5	31.0	9.3
W-3	200	111.0	132.6	40.0	18.6
W-4	225	98.7	115.0	43.0	17.3
W-4	275	90.3	104.0	42.0	21.3
		W-8 Vol % ThO_2·0.2 Wt % Na_2O[c]			
WD-43	38	--	199.4	0.9	1.3
WD-4	125	--	157.0	7.4	2.7
WD-42	175	--	160.6	3.0	1.3
WD-42	200	--	152.6	4.7	2.7
WD-42	225	--	152.5	25.0	6.7
WD-42	275	--	137.0	18.3	5.3
		W-8 Vol % ZrO_2·0.2 Wt % Na_2O[c]			
WD-37	38	--	203.5	3.8	4.0
WD-37	125	--	174.4	5.8	6.7
WD-38	175	--	164.0	0.5	1.3

(a) Reduction in area and elongation values are questionable due to inferior quality of the material as prepared for tensile testing.
(b) Stress-relief annealed 1 hour at 1200 C.
(c) Stress-relief annealed 1 hour at 1300 C.

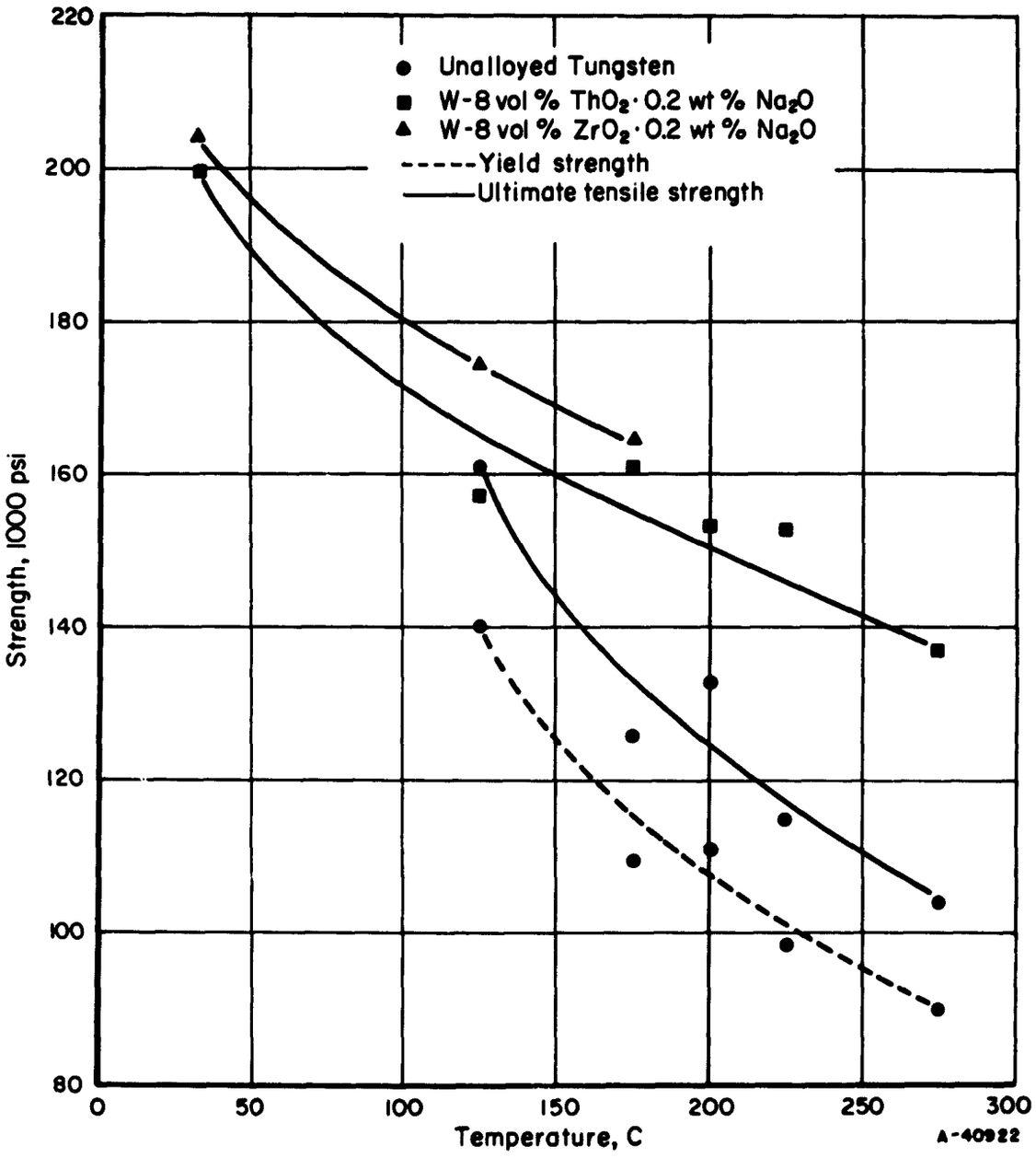


FIGURE 25. EFFECT OF TEMPERATURE ON THE STRENGTH PROPERTIES OF UNALLOYED TUNGSTEN AND THE 8 VOLUME PER CENT DISPERSOID ALLOYS OF THORIA AND ZIRCONIA, STRESS RELIEVED FOR 1 HOUR AT 1200 C

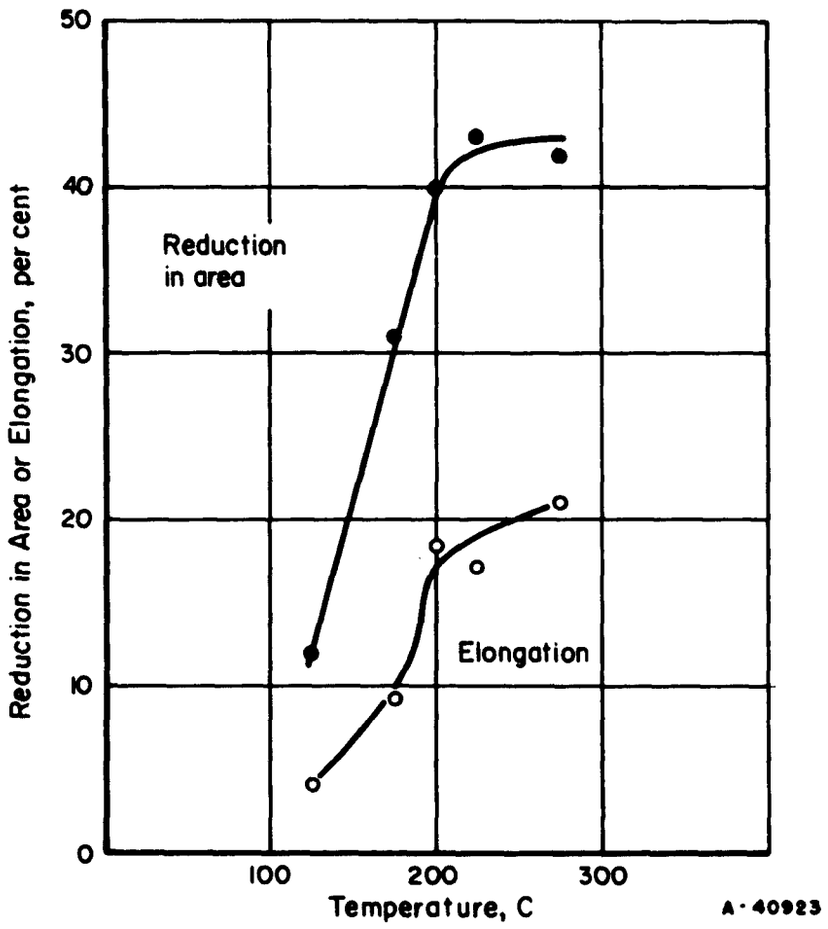


FIGURE 26. EFFECT OF TEMPERATURE ON THE TENSILE DUCTILITY OF UNALLOYED TUNGSTEN SHEET, STRESS RELIEVED FOR 1 HOUR AT 1200 C

As noted earlier, the absolute values of reduction in area and elongation obtained in tensile testing the thoria and zirconia alloys are questionable due to the poor physical condition of these test samples. However, it is of some interest to note that, despite the presence of internal notches (i.e., laminations), each of these alloy samples showed measurable evidence of some ductility (1 to 4 per cent elongation) at temperatures as low as 38 C.

SOLID-SOLUTION ALLOYS

Previous work[4] on arc-melted molybdenum-base alloys showed that additions of Groups VII and VIII metals resulted in hardness minima at low concentrations (less than 5 atom per cent) of these alloying elements. Similar effects were also indicated for additions of rhenium to tungsten and chromium. As discussed below, these effects are believed to result from the elimination of interstitial impurities, i.e., C, O, N, and H, from solid solution.

A plausible explanation of the reduced interstitial solubility comes from ideas proposed by Robins[5]. Robins based his ideas on the metallic bonding concept of Hume-Rothery[6] and Pauling that the bonding electrons resonate between neighboring atoms with the hybridized electronic structures of the transition metals having resonance between their s-p-d bonding orbital. Robins also used a suggestion by Kubachewski[7] that the coordination number for bcc metals may be taken to be twelve as opposed to a more commonly acceptable value of eight. The resonating covalent bond strength increases to a maximum when the number of bonding electrons equals half the coordination number, e.g., six resonating electrons in common with a coordination number of twelve. This most stable configuration then applies to the Group VI metals.

Robins has shown evidence that, when there are less than six electrons surrounding an atom, interstitial atoms tend to ionize and contribute electrons to the lattice. For the Group VIA metals, where maximum stability exists, the electron-contributing interstitials tend to segregate to point, line, and surface defects of lower coordination number, thereby relieving the electronic unbalance in these regions. Likewise, the contribution of electrons from a high valence metal (i.e., Group VII or VIII) should also be effective in this respect, while at the same time reducing the tolerance of the defect structure in general for interstitials.

In the present program, experiments were conducted to first verify and more accurately locate the existence of hardness minima in dilute tungsten-base alloys with the Groups VII and VIII metals. This was done with the intent of determining whether the same alloying effect which would lower hardnesses would also lower yield and tensile strengths. If so, this condition plus the absence of dislocation locking and strain hardening from interstitial atmospheres would be ideal for promoting ductility in such alloys at low temperatures.

As a matter of convenience, arc melting was elected as the method to be used for placement of the hardness minima in the tungsten alloys. The results of this work were later applied to alloys prepared using powder-metallurgical techniques.

Arc-Melted Alloys

Alloy Preparation and Metallography

Sixty-nine binary tungsten-base alloys were prepared containing additions of manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium, rhenium, osmium, iridium, and platinum in amounts from 0.1 through 10 atom per cent. All alloys were made from 10-gram-size compacted powder samples, of the appropriate compositions, which were arc melted under identical conditions in a water-cooled copper crucible. In addition, six control buttons of unalloyed tungsten were prepared using the same procedures.

Spectrographic chemical analyses were carried out on several selected binary alloys, in the as-cast condition, with the results shown in Table 11. Despite the short-time melting cycle used, melting losses of the iron, cobalt, and nickel additions were quite high. Retention of the platinum-group metal additions was roughly proportional to their vapor pressures. Thus, essentially all of the rhenium, osmium, and iridium additions were retained in melting, while only partial retention of the ruthenium, platinum, and rhodium was achieved during melting.

TABLE 11. ANALYTICAL DATA ON SELECTED BINARY TUNGSTEN-BASE ARC-MELTED ALLOYS

Metallic Addition	Alloy Content, atom per cent		Percentage of Recovery in Melting
	Nominal	Analyzed	
Fe	0.50	<0.003	Nil
Co	0.50	<0.003	Nil
Ni	1.00	<0.003	Nil
Ru	2.00	0.83	
Ru	3.00	0.82	27
Rh	1.00	0.072	7
Re	3.00	3.15	100
Os	1.00	0.87	87
Os	3.00	2.5	83
Ir	0.50	0.51	100
Pt	2.00	0.62	31
Pt	3.00	0.56	19

Metallographic examination of the as-cast alloy structures showed slight evidences of coring and/or incomplete solution of the solute element in some compositions. Accordingly, the remaining half of each ingot was given an 8-hour homogenization anneal in a vacuum atmosphere under a pressure of about 0.1 micron. Because of melting-point considerations, the manganese, iron, cobalt, and nickel compositions were annealed at 1400 C (2550 F) while the remaining alloys were homogenized at 2000 C (3630 F). In all cases, the homogenization anneals were effective in producing homogeneous, single-phase structures.

Hardness Evaluation

The Vickers hardness number was determined for each of the unalloyed controls and alloy buttons both as cast and after homogenization annealing. In all cases, at least five separate impressions were made on the individual samples using a 10-kg load.

All hardness-impression areas were examined metallographically for evidences of mechanical twin formation, but no twinning was observed in any of the cast or annealed ingots. However, slip bands were noticed around many hardness impressions on both the unalloyed and alloyed ingots.

Unalloyed Tungsten. The results of hardness measurements on the six unalloyed tungsten control buttons, as cast and after an 8-hour vacuum anneal at 2000 C, are summarized in Table 14.

As arc melted, the average hardnesses of the six control ingots ranged from 356 to 369 VHN with a mean value of 363 VHN and an average deviation of ±7 VHN. However, after an 8-hour vacuum anneal at 2000 C, the hardness of each of these control buttons decreased significantly to values ranging from 336 to 354 VHN with a mean value of 343 VHN ± 7 VHN. This decrease in hardness was interpreted primarily as a softening effect resulting from partial removal of interstitials (most probably carbon and/or oxygen) retained in the arc-melted ingots. Unfortunately, these samples were too small to yield reliable analytical data. However, prior experience has shown that appreciable purification of tungsten from interstitials can be effected by vacuum arc melting and/or annealing. In this connection, it is of interest to note that the mean hardness value of 343 VHN obtained on the vacuum-annealed button ingots compares favorably with the lowest hardness values reported* for massive tungsten metal.

Solid-Solution Alloys. The average hardness of each of the binary-alloy ingots as cast and after homogenization is listed in Tables 12 and 13.

As cast, definite minima were indicated in the hardness curves for all of the binary-alloy systems, except the W-Mn and W-Pd, where at least 0.25 atom per cent of the alloying addition was retained. Vacuum annealing did not significantly affect the hardnesses of the alloys. However, since the unalloyed tungsten base showed a hardness drop of about 20 VHN on annealing, the magnitude of the softening effect on the annealed alloy ingots was not as great as for the cast condition. Table 14 lists the maximum hardness decreases observed in each of the binary alloy series and indicates the concentration of each alloying addition required for this effect.

The presence of the hardness minimum is taken as a net effect of a reduction of interstitial hardening through reduced interstitial solubility and increased alloy solid-solution hardening. The position of the minimum is believed to have no significance other than to indicate differences in solid-solution hardening for the various elements.

* The Vickers hardness numbers measured on a series of tungsten single crystals, prepared by electron-beam zone purification of powder-metallurgy rod, ranged from 338 to 354 VHN after one to seven zone-refining passes.[2]

TABLE 12. HARDNESS DATA FOR THE AS-CAST SOLID-SOLUTION ALLOYS

Binary System	Vickers Hardness Number[a] for Indicated Nominal Atomic Per Cent Solute									
	0.10	0.30	0.50	1.0	1.5	2.0	3.0	4.0	5.0	10.0
W-Mn	356	355	365	366	--	--	354	--	--	--
W-Fe	360	348	347	353	--	--	362	--	363	--
W-Co	344	346	343	350	--	--	354	--	354	--
W-Ni	352	361	356	350	--	--	361	--	360	--
W-Ru	364	367	358	370	--	318	341	--	408	--
W-Rh	352	363	356	346	--	340	354	--	350	--
W-Pd	354	359	356	356	--	--	359	--	--	--
W-Re	346	354	349	352	--	--	330	306	303	332
W-Os	356	340	318	310	320	368	426	--	--	--
W-Ir	346	340	334	389	--	--	669	--	--	--
W-Pt	356	362	350	350	--	313	335	--	529	--

(a) 10-kg load.

TABLE 13. HARDNESS DATA FOR AS-CAST SOLID-SOLUTION ALLOYS AFTER HOMOGENIZATION[a]

Binary System	Vickers Hardness Number[b] for Indicated Nominal Atomic Per Cent Solute									
	0.10	0.30	0.50	1.0	1.5	2.0	3.0	4.0	5.0	10.0
W-Mn	345	354	349	352	--	--	359	--	--	--
W-Fe	336	340	349	343	--	--	358	--	375	--
W-Co	343	337	347	350	--	--	348	--	366	--
W-Ni	344	345	335	358	--	--	361	--	360	--
W-Ru	341	363	350	339	-	304	323	--	404	--
W-Rh	352	352	353	343	--	359	347	--	381	--
W-Pd	343	357	356	351	--	--	366	--	--	--
W-Re	351	351	345	345	--	--	330	314	293	330
W-Os	342	331	330	304	330	360	428	--	--	--
W-Ir	342	316	318	376	--	--	745	--	--	--
W-Pt	357	351	350	356	--	315	344	--	374	--

(a) All ingots homogenized by vacuum annealing 8 hours at 1400 C (for the W-Mn, W-Fe, W-Co, and W-Ni alloys) or 2000 C (for the W-Ru, W-Rh, W-Pd, W-Re, W-Os, W-Ir, and W-Pt alloys).

(b) 10-kg load.

TABLE 14. SOFTENING EFFECTS OF HIGH-VALENCY METAL ADDITIONS IN ARC-MELTED TUNGSTEN

Addition Element	Group	Long Period No.	Total of (d + s) Electrons	Optimum Concentration, atom per cent[a]	Maximum Softening Effect, VHN	
					As Cast[b]	As Annealed[c]
(100 W)	VI	3	6	--	--	--
Re	VII	3	7	5.00	60	50
Os	VIII-A	3	8	0.87	53	39
Ir	VIII-B	3	9	0.30	29	27
Pt	VIII-C	3	10	0.62	49	28
Ru	VIII-A	2	8	0.83	45	39
Rh	VIII-B	2	9	(2.00)	23	nil
Pd	VIII-C	2	10	--	nil	nil
Mn	VII	1	7	--	nil	nil
Fe	VIII-A	1	8	(0.10)	16	7
Co	VIII-B	1	9	(0.10-0.50)	20	6
Ni	VIII-C	1	10	(1)	13	8

(a) Values in parenthesis are nominal; all others are analyzed.
(b) Referred to base hardness of 363 VHN for unalloyed controls.
(c) Referred to base hardness of 343 VHN for unalloyed controls.

As shown in Table 14, the greatest softening effect was obtained with Groups VII and VIII alloying elements in the third long period of which tungsten is a member. Progressively less softening was obtained with the Groups VII and VIII metals for the second and first long periods, respectively. Also, within a given period, the most effective alloying elements were those with the least number of valency electrons (i.e., total d + s electrons) above six, the number of valency electrons for tungsten. Specifically, ruthenium, platinum, iridium, osmium, and rhenium showed the greatest softening effects and, in the approximate order listed, were increasingly effective in lowering the hardness of tungsten by as much as 60 VHN.

These results suggest that the softening of unalloyed tungsten effected by the Groups VII and VIII metal additions is not simply a direct function of the number of valency electrons contributed by each, as postulated earlier. Rather, the greater effects of those additions in the same long period as tungsten suggests that the relative energy level of the electrons introduced with the solute element is perhaps of at least equal significance.

One further observation of interest was made regarding the W-Re, W-Os, and W-Ir alloys. This comes from an extrapolation of the hardness curves for these alloys, beyond the minimum concentrations required for maximum softening, to zero solute content, as shown in Figure 27. As indicated, all three curves converged to a common origin at a Vickers hardness of 242 ± 12 VHN, which suggests that this value represents the true hardness of pure tungsten.

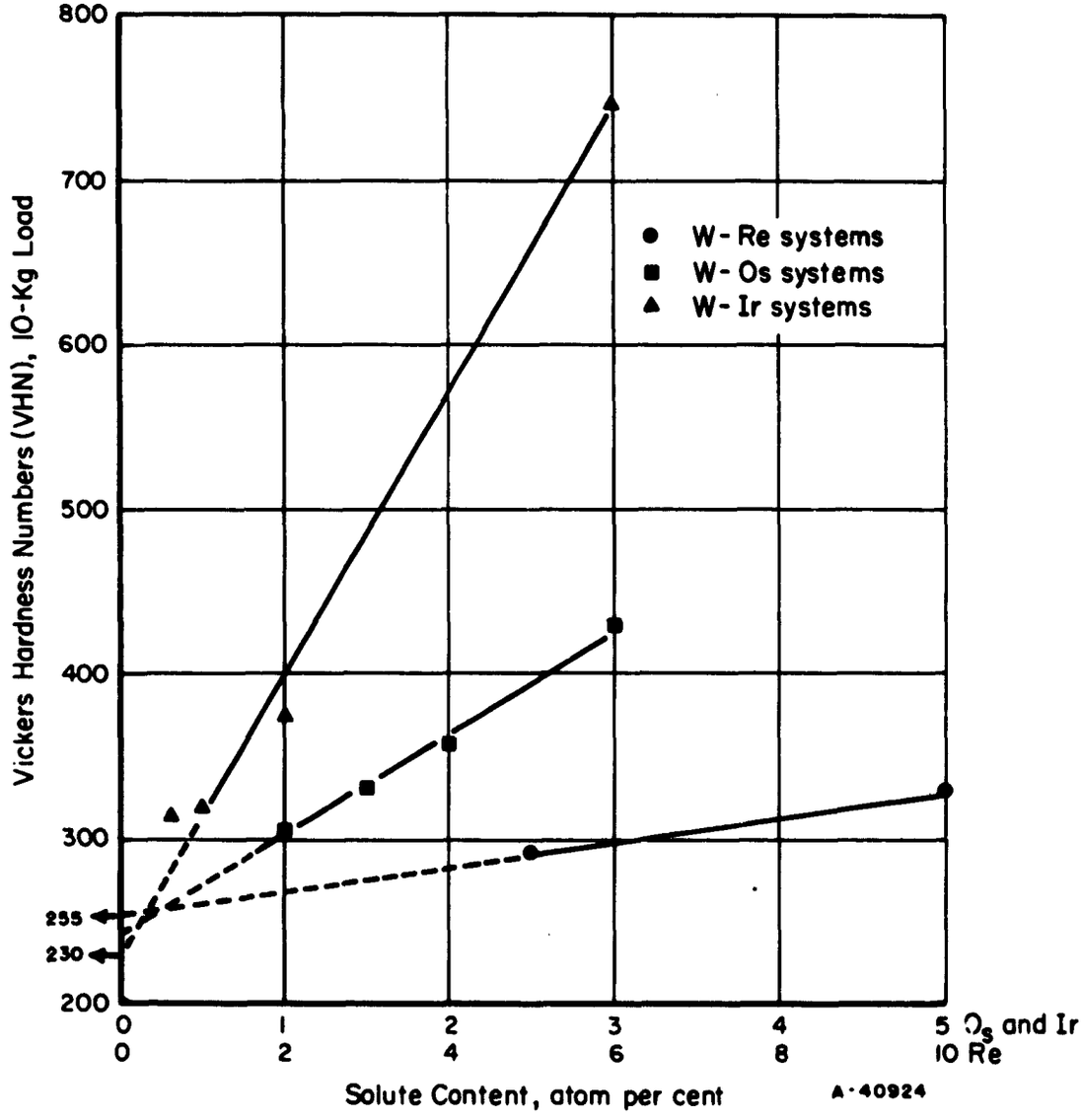


FIGURE 27. EXTRAPOLATIONS BEYOND THE MINIMUM CONCENTRATIONS GIVING MAXIMUM SOFTENING FOR THE ARC-MELTED AND HOMOGENIZED SOLID-SOLUTION ALLOYS

Powder-Metallurgy Alloys

As a follow-up to the arc-melted alloy studies, two groups of metallic-addition binary alloys were prepared using powder-metallurgical techniques. The first group consisted of the seven binary W-Fe, W-Co, W-Ru, W-Re, W-Os, W-Ir, and W-Pt alloys which had shown the lowest as-cast hardnesses. When gross segregation was later discovered in these alloys, a second group was prepared. As a matter of expediency, the second group consisted only of those five binary alloys which showed the greatest softening effects. The details of these experiments are summarized below.

Compact Preparation, Sintering, and Fabrication

The compositions in the first group of alloys prepared are listed in Table 15. Each of these was prepared to a total weight of 160 grams by adding appropriate amounts of the alloy powders to the unalloyed-tungsten powder and cone blending the mixture for 5 hours prior to compaction.

Compaction was accomplished by mechanically pressing each powder charge in 1/4 x 1/2 x 7-inch bars as previously described. All of the compacts were then presintered for 2-hours at 1200 C with the resultant densities ranging from 54.3 to 64.6 per cent of theoretical.

Sintering was carried out for 4 hours at 2300 C, using self-resistance heating under a vacuum atmosphere. Those alloys of tungsten with Fe, Co, Pt, and Ru all exhibited melting-point minima below the desired sintering temperature, 2300 C. Therefore, to effect alloying of these elements without incipient melting, an "alloying stage" was incorporated into the normal sintering schedule. This involved the following generalized heating sequence:

(1) Heat to 1000 C and outgas for 1 hour

(2) Increase temperature to 50 C below the melting-point minimum and hold for 30 minutes

(3) Increase temperature to the melting-point minimum and hold for 30 minutes

(4) Increase temperature to 50 C above the melting-point minimum and hold for 30 minutes

(5) Increase temperature to 2300 C and hold for 4 hours.

Selected alloys from the first group were analyzed spectrographically for their alloy retentions after sintering. As can be seen from Table 16, all of the alloys within this group were near the desired optimum compositions except those containing Ru and Pt. Analytical data accumulated for these compositions showed a higher retention of these elements during sintering than was anticipated on the basis of retention after melting (see Table 16).

Fabrication by rolling was attempted under conditions identical to those previously described for the dispersoid alloys (see Table 3) and was only partially successful on three out of the eight alloys, i.e., W-0.50Fe, -1.00Os, and -0.30Ir. Metallographic examination showed that each of these alloys was grossly segregated; hence their poor fabricability was generally ascribed to the inhomogeneous microstructures.

TABLE 15. ALLOY COMPOSITIONS, SINTERING CONDITIONS, AND DENSITIES OF THE POWDER METALLURGY-SOLID SOLUTION ALLOYS

Alloy	Alloy Content, atom per cent		Sintering Conditions		Alloy Density		
	Added	Intended	Time, hr	Temperature, C	Theoretical[a], g/cm^3	Per Cent of Theoretical	
						Initial[b]	Final
				Group 1			
WS-1	0.50Fe	0.10Fe	4	2300	19.29	64.6	92.7
WS-2	0.50Co	0.10Co	4	2300	19.29	62.8	90.2
WS-6	2.00Ru	0.83Ru	4	2300	19.20	58.3	94.0
WS-3[c]	3.00Ru	1.00Ru	4	2300	19.19	60.6	93.5
WS-4	5.00Re	5.00Re	4	2300	19.39	54.7	93.0
WS-5	1.00Os	0.87Os	4	2300	19.33	54.3	92.8
WS-8	0.30Ir	0.30Ir	4	2300	19.31	56.0	88.1
WS-7	2.00Pt	0.62Pt	4	2300	19.34	59.5	88.0
				Group 2			
WS-9	5.00Re	5.00Re	2	2600	19.39	57.6	94.5
WS-10	1.03Ru	0.83Ru	2	2600	19.29	65.5	93.6
WS-11	1.02Os	0.87Os	2	2600	19.33	55.9	94.8
WS-12	0.30Ir	0.30Ir	2	2600	19.31	56.5	94.3
WS-13	0.64Pt	0.62Pt	2	2600	19.31	67.4	93.0

(a) Calculated using the relationship $\frac{1}{d} = \frac{wt\%A}{100d_a} + \frac{wt\%B}{100d_b} + \cdots$, where d values for W, Fe, Co, Ru, Os, Ir, and Pt were taken as 19.30, 7.87, 8.85, 12.2, 21.04, 22.57, 22.5, and 21.45 g/cm^3, respectively.

(b) Refers to density achieved after pressing under 50,000 psi and presintering for 2 hours in a dry hydrogen atmosphere.

(c) Vacuum radiation sintered. All other bars sintered by self-resistance heating.

TABLE 16. SUMMARY OF ANALYTICAL DATA COLLECTED FROM SELECTED FIRST-GROUP ALLOYS VACUUM SINTERED FOR 4 HOURS AT 2300 C

Alloy	Binary System	Alloy Content, atom per cent			Per Cent Retention
		Prepared	Analyzed[a]	Optimum[b]	
WS-4	W-Re	5.00	(5.00)	5.00	(100)
WS-6	W-Ru	2.00	1.62	0.83	81
WS-5	W-Os	1.00	0.87	0.87	85
WS-8	W-Ir	0.30	(0.30)	0.30	(100)
WS-7	W-Pt	2.00	2.02	0.62	100

(a) Values in parentheses estimated on the basis of previous work.

(b) Alloy contents corresponding to observed hardness minima previously determined for the respective binary systems.

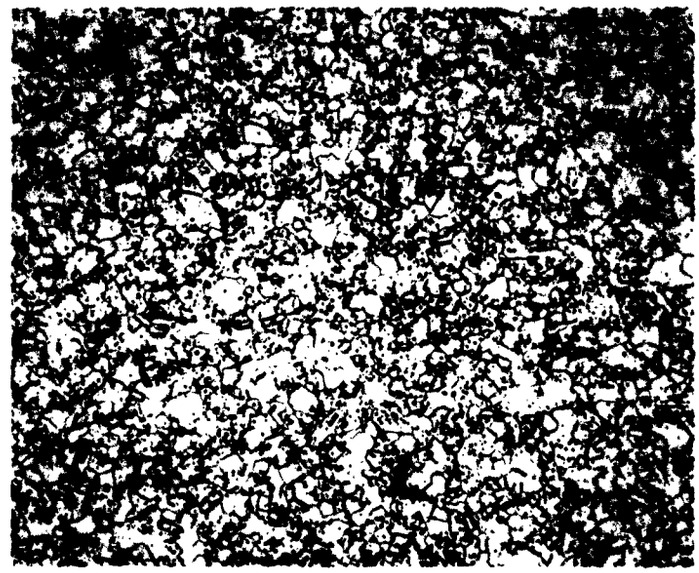
Compositions for the five second-group alloys were selected on the basis of the analytical data obtained from the first group of alloys after sintering and are presented in Table 16. From these data, weight-loss compensations were applied to the initial preparation of the necessary second-group compositions, W-1.03Ru and W-1.02Os, so as to obtain their respective optimum alloy contents after sintering, i.e., W-0.83Ru and W-0.87Os.

An improved consolidation practice which involved both better blending and sintering techniques was applied to these materials. Beginning with the alloying powders, minus 325-mesh fines were screened from each commercial lot. Homogeneous-alloy-powder charges were then accomplished by cone blending for 5 hours while proportionally increasing the unalloyed-tungsten-powder content in each charge up to the required amount. All five of the second-group alloys were then sintered for 2 hours at 2600 C using the delayed heating schedule described earlier. This resulted in homogeneous compositions as shown in Figure 28 which compares the structure of the W-5.00Re alloy with that of unalloyed tungsten.

Fabrication conditions were similar to those previously applied to both the dispersoid alloys and the first-group solid-solution alloys. The only exception was an insurance step taken to effect more complete solution of the alloying elements in those bars surviving breakdown rolling at 1800 C. This involved an annealing treatment of 90 minutes at 1800 C. Following this, rolling as usual at temperatures ranging from 1600 C to 1200 C produced 35-mil strip.

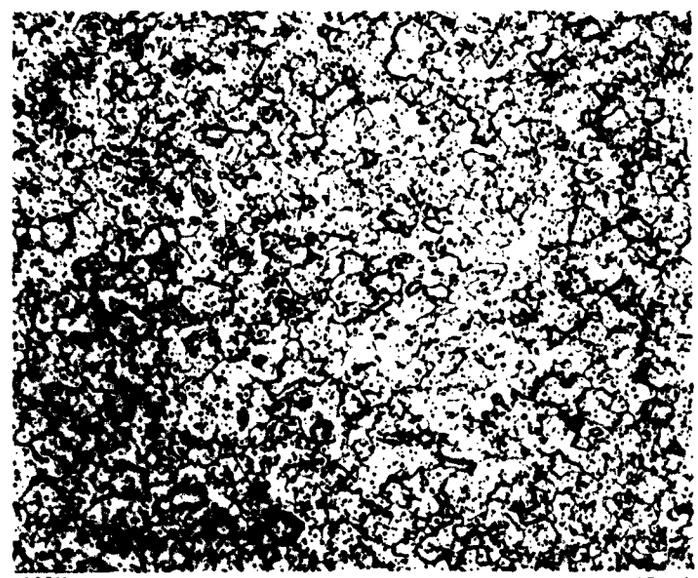
Three of the alloys, i.e., W-5.00Re, 1.02Os, and 0.30Ir fabricated to excellent quality strip as a result of the improvements in processing applied to those second-group materials. However, both the W-1.03Ru and W-0.64Pt compositions broke up during initial rolling at 1800 C, and no material was recovered from either alloy.

Chemical analyses were performed on representative wrought samples of unalloyed tungsten and the three optimum solid-solution alloys. Spectrographic, conductometric, and vacuum-fusion techniques, respectively, were used to determine the metallics, carbon, and gaseous interstitials. Table 17 summarizes the results.



100X N87115

a. WS-9, W-5.00Re
(94.5% dense)



100X N87114

b. W-5, 100W
(94.7% dense)

FIGURE 28. MICROSTRUCTURES SHOWING THE HOMOGENIETY ACHIEVED IN THE W-5.00Re ALLOY COMPARED WITH THAT OF UNALLOYED TUNGSTEN AFTER SINTERING FOR 2 HOURS AT 2600 C

Murakami's etch.

TABLE 17. CHEMICAL ANALYSES OF UNALLOYED TUNGSTEN AND THE THREE BINARY SOLID-SOLUTION ALLOYS

Alloy	Nominal Alloy Content, atom per cent	Impurity Elements, ppm											
		Si	Mg	Cr	Fe	Ni	Mo	Cu	Ca	Al	C(a)	O(b)	H(c)
W-2	100W	20	<5	<40	40	<10	30	<3	11	<10	10	17.9	0.8
WS-9	5.00Re	--	--	--	--	--	--	--	--	--	10	5.8	0.3
WS-11	1.02Os	<10	<3	<40	40	<10	30	<3	<3	<10	10	3.1	0.4
WS-12	0.30Ir	<10	<3	<40	40	<10	25	<3	<3	<10	10	2.4	0.3

(a) Precision = ±10 ppm.
(b) Precision = ±0.2 ppm.
(c) Precision = ±0.02 ppm.

With the limitations in accuracy of the analytical techniques used, it was not possible to detect any significant differences in the level of metallic impurities or carbon content between the unalloyed control and any of the three alloys. However, the data of Table 17 show that each of the three alloys contained only about one-third as much oxygen (2.4 to 5.8 ppm compared with 17.9 ppm) and one-half as much hydrogen (0.3 to 0.4 ppm compared with 0.8 ppm) as the unalloyed control. These data thus stand in support of the belief that one of the most beneficial effects of adding high-valency metals to tungsten is to reduce the solubility of tungsten for interstitial impurities.

Softening, Recrystallization, and Grain-Growth Behaviors

Softening and recrystallization studies were carried out on wrought samples of the three fabricable solid-solution alloys, i.e., W-5.00Re, 1.02Os, and 0.30Ir.

Samples from each material were annealed for 1 hour at temperatures from 1000 C through 2300 C. After annealing, the microstructures of these alloys were examined for evidence of recrystallization, and from these observations the respective 1-hour recrystallization temperatures were determined to within 100 C.

Vickers hardnesses were determined on all of the samples and are summarized in Table 18. This table also includes hardness data taken from samples of all the materials after the intermediate- and finish-rolling stages.

During fabrication, the hardnesses of the alloys increased progressively. Comparisons of as-wrought hardness values after first-stage intermediate rolling at 1600 C showed the alloys to be 17 to 37 VHN softer than unalloyed tungsten, however, after finish rolling at 1200 C, the hardness of the alloys ranged from 11 to 23 VHN higher than that of unalloyed material. These data reflect tendencies for the alloys to strain or work harden more rapidly than unalloyed tungsten during fabrication.

Figure 29 illustrates the softening characteristics for unalloyed tungsten and the three optimum fabricable solid-solution alloys. Generally, the shapes of all the softening curves were similar. For each material, the hardness decreased gradually with increasing annealing temperatures up to 1400 C then dropped off rapidly over the range

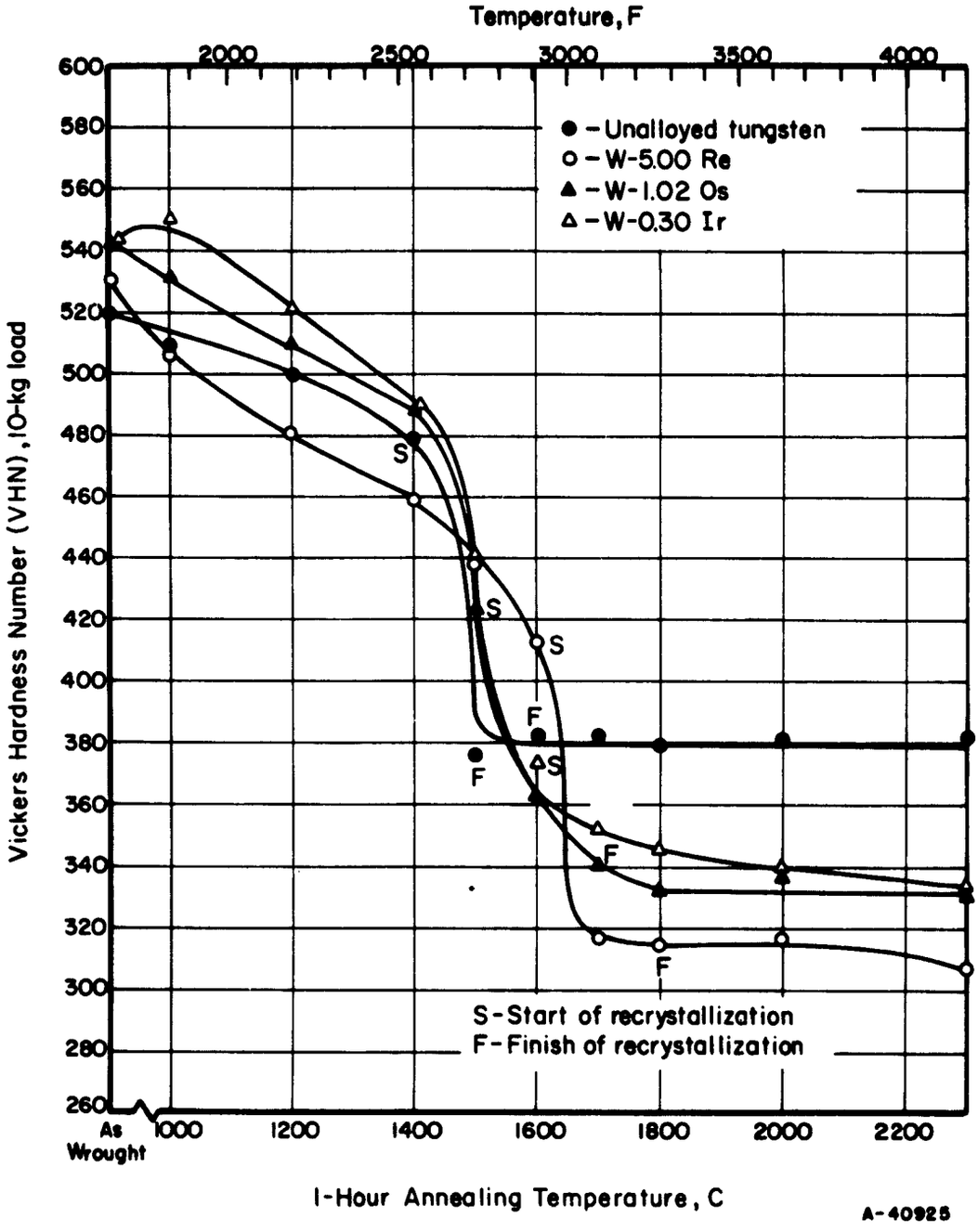


FIGURE 29. SOFTENING CURVES FOR WROUGHT UNALLOYED TUNGSTEN AND THE THREE OPTIMUM POWDER METALLURGY-SOLID SOLUTION ALLOYS

TABLE 18. EFFECT OF FABRICATION AND ANNEALING ON THE MICROHARDNESS OF UNALLOYED TUNGSTEN AND THE POWDER-METALLURGY SOLID-SOLUTION ALLOYS

Alloy	Nominal Alloy Content, Weight Per Cent	Nominal Alloy Content, Atomic Per Cent	Vickers Hardness Numbers (VHN), 10-Kg Load: Rolled 1600 C, Annealed 1400 C	Rolled 1400, C Annealed 1200 C	As-Wrought, Rolled 1200 C	1-Hour Vacuum-Annealing Temperature, C: 1000	1200	1400	1500	1600	1700	1800	2000	2300
Unalloyed Tungsten														
W-5	100W	100W	450	483	519	508	499	479	376	383[a]	383[a]	380[a]	382[a]	385[a]
Solid-Solution Alloys														
WS-9	5.06Re	5.00Re	413	455	530	506	480	459	438	413	317	315[a]	317[a]	308[a]
WS-11	1.05Os	1.02Os	417	464	542	531	511	489	423	374	340[a]	333[a]	337[a]	331[a]
WS-12	0.31Ir	0.30Ir	433	454	542	550	521	490	448	364	352[a]	347[a]	340[a]	334[a]

(a) Fully recrystallized microstructures.

TABLE 19. SUMMARY OF RECRYSTALLIZATION OBSERVATIONS MADE ON UNALLOYED TUNGSTEN AND THE POWDER-METALLURGY SOLID-SOLUTION ALLOYS

Alloy	Nominal Alloy Content, Weight Per Cent	Nominal Alloy Content, Atomic Per Cent	1-Hour Recrystallization Temperature, C: Start (S)	Finish (F)	Recrystallization Range, ΔC
W-5	100W	100W	1400	1600	200
WS-9	5.06Re	5.00Re	1600	1800	200
WS-11	1.05Os	1.02Os	1500	1700	200
WS-12	0.31Ir	0.30Ir	1600	1600	<100

1500 C to 1800 C. At higher temperatures the hardnesses leveled off and approached constant values.

The beginning and finish of recrystallization are denoted on each curve in Figure 29 by S and F and are tabulated for each alloy in Table 19. Comparison with unalloyed tungsten which recrystallized over a 200-degree interval from 1400 C to 1600 C showed all three of the alloys to have higher recrystallization temperatures. Both the W-5.00Re and W-1.02Os alloys recrystallized over 200-degree intervals with respective starting temperatures of 1600 C and 1500 C and respective finishing temperatures of 1800 C and 1700 C. The W-0.30Ir alloy was unique in that it recrystallized very abruptly over a narrow temperature range close to 1600 C. From this work with the powder metallurgy-solid solution alloys it is significant to note that the highest 1-hour temperature for complete recrystallization, 1800 C, was observed for the W-5.00Re alloy.

Another point of importance was revealed by comparing the softening effects (ΔVHN) achieved in the powder-metallurgy solid-solution alloys with those obtaining in arc melting. The pertinent data are given in Table 20. As shown, the relative softening effects of rhenium, osmium, and iridium in the powder-metallurgy alloys are in the same order as those obtained in arc melting. Thus, rhenium gives the greatest effect and iridium the least. The absolute hardness values of the powder-metallurgy alloys were slightly greater (15 to 27 VHN) than when these same alloys were arc melted and vacuum annealed 8 hours at 2000 C. Nevertheless, the magnitude of the softening effect for each of the alloy additions was greatest when the alloys were made using powder-metallurgical techniques.

TABLE 20. COMPARISON OF SOFTENING EFFECTS FOR THE POWDER-METALLURGY AND ARC-MELTED SOLID-SOLUTION ALLOYS

Optimum Alloy Content, atomic per cent	Powder-Metallurgy Alloys(a)		10-G Arc-Melted Ingot Alloys		
		Softening Effect, ΔVHN		Softening Effect, ΔVHN	
	VHN		VHN(b)	As Cast(c)	Annealed(d)
W-5.00Re	308	75	293	60	50
W-0.87Os	331	52	304	53	39
W-0.30Ir	334	49	316	29	27

(a) Referred to a value of 383 VHN for powder-metallurgy unalloyed tungsten obtained for a common annealing condition of 1 hour at 2300 C.

(b) Values obtained from alloy melted and vacuum annealed for 8 hours at 2000 C.

(c) Referred to a value of 363 VHN for as-cast unalloyed tungsten.

(d) Referred to a value of 343 VHN for as-cast and vacuum annealed (8 hours at 2000 C) unalloyed tungsten.

This apparent contradiction arises from referring the hardness of the individual alloys to the hardness of the respective unalloyed tungsten control samples used. Thus the hardness of the unalloyed tungsten-base material varied with processing as follows:

Process Treatment	Hardness, VHN
Pressed, sintered, rolled, and vacuum annealed 1 hour at 2300 C	383
Arc melted	363
Arc melted and vacuum annealed 8 hours at 2000 C	343

Taken collectively, the data of Table 20 show:

(1) That the hardness of tungsten and each of the three alloys, consolidated by powder metallurgy techniques, is progressively decreased by arc melting and vacuum annealing, respectively.

(2) That irrespective of the consolidation method used, alloying of the tungsten with small amounts of rhenium, osmium, and iridium provides an additional, significant increment of softening (and purification).

The grain size of each fully recrystallized microstructure resulting from the softening and recrystallization studies was determined, and these grain sizes are tabulated in Table 21 along with the approximate 1-hour recrystallization temperatures.

Figure 30 illustrates the effect of increasing 1-hour annealing temperature on grain size. As shown, comparable rates of grain growth were obtained for both unalloyed tungsten and the W-5.00Re alloy which were reflected by the similarity in slope of their respective curves. Equivalent, but appreciably more rapid, grain growth rates were obtained for the W-1.02Os and W-0.30Ir alloys.

All three of the alloying elements promoted grain refinement after annealing for 1 hour at the minimum temperature for complete recrystallization. This was demonstrated by grain sizes of 4200, 4000, and 1775 grains/mm^2 which were obtained for the W-0.30Ir, W-1.02Os and W-5.00Re alloys, respectively, in comparison with 1162 grains/mm^2 achieved for unalloyed tungsten. Each of the alloys recrystallized to equiaxed microstructures as shown in Figure 31. However, subsequent annealing of the W-1.02Os and W-0.30Ir alloys at 2300 C resulted in exaggerated growth of some grains [illustrated in Figure 32, a(4) and b(4)] which gave rise to structures of widely variant grain size.

Bend Transition Temperature

Individual bend specimens were cut from each of the four as-wrought solid-solution alloys including unalloyed tungsten and prepared in accordance with the procedure previously described for the dispersoid alloys. Smooth bright surfaces resulted for the unalloyed tungsten and the W-5.00Re alloy after polishing; however the surfaces of both the W-1.02Os and W-0.30Ir alloys pitted badly.

The samples were tested according to the same procedure applied to the dispersoid alloys and ductility was expressed in terms of T-values.

TABLE 21. SUMMARY OF RECRYSTALLIZATION TEMPERATURES AND THE EFFECT OF HIGH-TEMPERATURE ANNEALING ON THE GRAIN SIZE OF UNALLOYED TUNGSTEN AND THE THREE OPTIMUM SOLID-SOLUTION ALLOYS

Alloy	Nominal Alloy Content		Approximate 1-Hour Recrystallization Temperature, C	Grain Size, grains/mm^2 1-Hour Vacuum Annealing Temperature, C				
	Weight Per Cent	Atom Per Cent		1600	1700	1800	2000	2300
			Unalloyed Tungsten					
W-1	100W	100W	1600	1000	--	1175	650	--
W-4	100W	100W	1600	975	--	1150	775	175
			Solid-Solution Alloys					
WS-9	5.06Re	5.00Re	1800	--	--	1775	1275	650
WS-11	1.05Os	1.02Os	1700	--	4000	3100	1900	<100
WS-12	0.31Ir	0.30Ir	1700	4200	3025	1925	925	<100

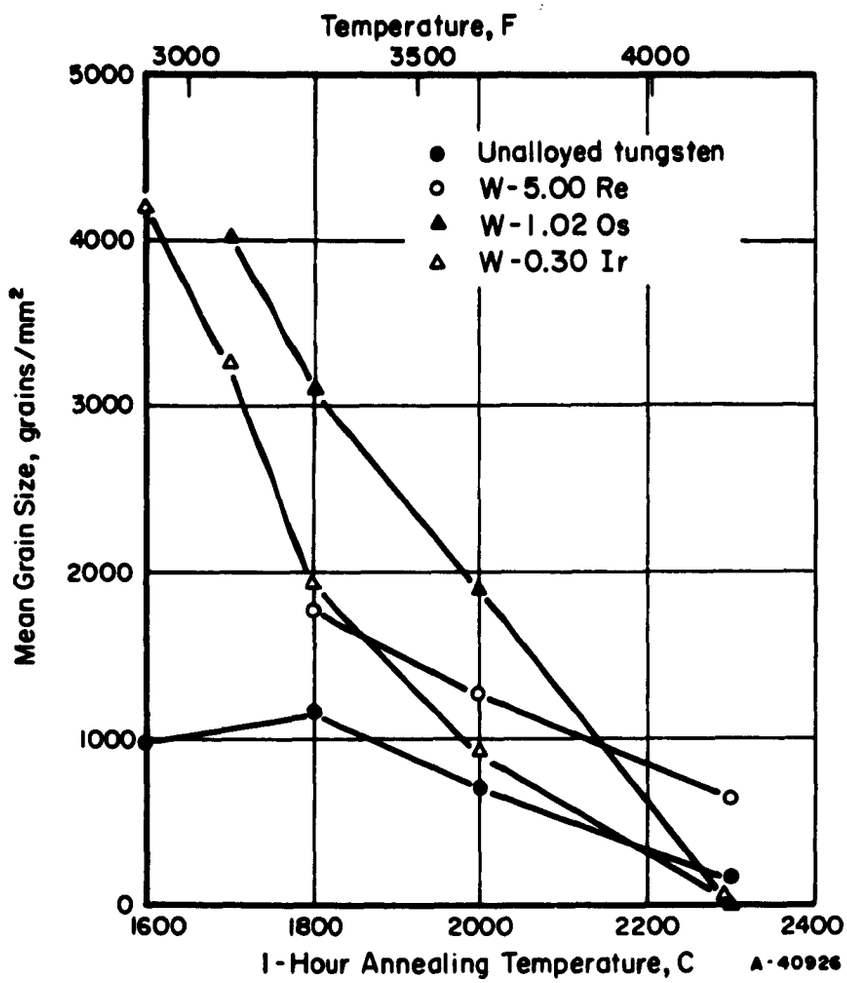
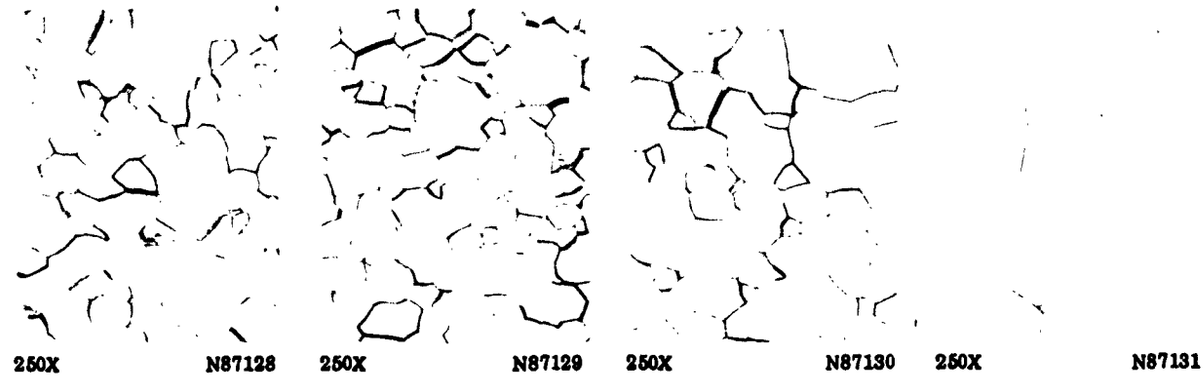


FIGURE 30. GRAIN-GROWTH BEHAVIOR OF UNALLOYED TUNGSTEN AND THE THREE OPTIMUM POWDER METALLURGY-SOLID SOLUTION ALLOYS

250X N87132 250X N87134 250X N87135 250X N87136

(1) 1600 C, 4200 grains/mm^2 (2) 1800 C, 1925 grains/mm^2 (3) 2000 C, 925 grains/mm^2 (4) 2300 C, <100 grains/mm^2

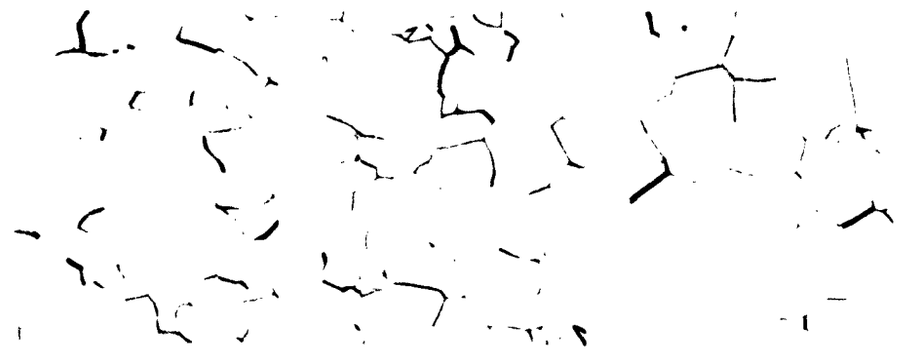
a. WS-12, W-0.30Ir



250X N87128 250X N87129 250X N87130 250X N87131

(1) 1700 C, 4000 grains/mm^2 (2) 1800 C, 3100 grains/mm^2 (3) 2000 C, 1900 grains/mm^2 (4) 2300 C, <100 grains/mm^2

b. WS-11, W-1.02Os



250X N87125 250X N87126 250X N87127

(1) 1800 C, 1775 grains/mm^2 (2) 2000 C, 1275 grains/mm^2 (3) 2300 C, 650 grains/mm^2

c. WS-9, W-5.00Re

FIGURE 31. LONGITUDINAL MICROSTRUCTURES OF THE 3 POWDER METALLURGY-SOLID SOLUTION ALLOYS ILLUSTRATING STRUCTURAL CHANGES OCCURRING AFTER ANNEALING 1 HOUR AT THE INDICATED TEMPERATURES

Murakami's etch.

Table 22 summarizes the results of eight bend-transition-temperature determinations completed on this group of materials. Two 1-hour annealing conditions of 1200 C and 1800 C were investigated for each alloy. Stress relieving was accomplished by annealing at 1200 C, while annealing at 1800 C effected complete recrystallization in all of the materials.

TABLE 22. SUMMARY OF DUCTILE-TO-BRITTLE BEND TRANSITION TEMPERATURES FOR UNALLOYED TUNGSTEN AND THE SOLID-SOLUTION ALLOYS

Alloy	Nominal Alloy Content, Weight Per Cent	Nominal Alloy Content, Atomic Per Cent	1-Hour Annealing Temperature, C	8T Transition Temperature, C	8T Transition Temperature, F	4T Transition Temperature, C	4T Transition Temperature, F
			Unalloyed Tungsten				
W-5	100W	100W	1200	200	392	215	419
			1800	400	752	--	--
			Solid-Solution Alloys				
WS-9	5.06Re	5.00Re	1200	165	329	175	347
			1800	295	563	--	--
WS-11[a]	1.05Os	1.02Os	1200	210	410	210	410
			1800	>450	>842	--	--
WS-12[a]	0.31Ir	0.30Ir	1200	>400	>752	--	--
			1800	>450	>842	--	--

(a) Badly pitted after electropolishing.

This work showed that the transition temperatures of the three alloys were in the same order as their relative softening effects. Thus, the W-5.00Re alloy had the lowest transition temperatures with the W-1.02Os and W-0.30Ir alloys showing progressively higher transitions, for both the wrought and recrystallized test conditions. Specifically, reductions in the transition temperatures of 35 C and 105 C, respectively, were obtained for the stress-relieved and recrystallized conditions of the W-5.00Re alloy.

The improvements in ductility achieved with the W-5.00Re alloy reflected the anticipated effect of alloying the Groups VII and VIII metals with tungsten to eliminate interstitial impurities from solution, thereby reducing the yield strength of the material and improving its ductility.

DISPERSOID-SOLID SOLUTION ALLOYS

Table 23 lists a group of five ternary dispersoid-solid solution alloys which were prepared with the objective of combining the beneficial effects of both metallic solutes and dispersions. Three of the five contained 2, 4, and 8 volume per cent thoria dispersed in a W-5.00Re matrix, while the other two alloys contained 8 volume per cent thoria dispersed in matrices of W-1.02Os and W-0.30Ir, respectively.

Compact Preparation, Sintering, and Fabrication

The dispersoid-solid solution alloys were prepared by combining the best procedures established for the separate preparation of dispersoid and solid-solution alloys discussed in earlier sections. Thus, the thoria and Na_2O were first introduced aqueously, then evaporated and baked to dryness. Next, fines (-325 mesh) of the metallic powders were progressively added and blended with the thoriated powder until the total compact weight of 160 grams was achieved.

Consolidation was accomplished by mechanically pressing each powder charge into 1/4 x 1/2 x 7-inch bars. Each compact was then presintered for 2 hours at 1200 C, which resulted in densities ranging from 49.3 to 56.0 per cent of theoretical.

A uniform sintering treatment of 2 hours at 2600 C was initially applied to each compact. However, as shown in Table 23, two of these alloys, W-5.00Re and W-0.30Ir, each containing 8 volume per cent thoria, required resintering to obtain a satisfactory density for fabrication.

Fabrication conditions were identical to those previously described and applied to the second-group solid solution alloys. The W-5.00Re alloys containing 2 and 4 volume per cent thoria rolled to excellent quality strip, while the 8 volume per cent composition laminated and edge cracked beyond recovery during breakdown rolling. Both of the W-1.02 Os and W-0.30Ir alloys containing 8 volume per cent thoria also displayed poor fabricability during rolling, as only partial recovery of each of these materials was achieved after finish rolling.

Softening, Recrystallization, and Grain-Growth Behaviors

Softening and recrystallization studies were carried out on wrought samples of the four dispersoid-solid solution alloys, i.e., W-5.00Re-2 volume per cent ThO_2, W-5.00Re-volume per cent ThO_2, W-1.02Os-8 volume per centThO_2, and W-0.30Ir-8 volume per cent ThO_2.

Samples from each alloy were annealed for 1 hour at temperatures from 1000 C through 2300 C. After annealing, the microstructures of these materials were examined for evidence of recrystallization, and from these observations the respective 1-hour recrystallization temperatures were determined to within 200 C.

TABLE 23. ALLOY COMPOSITIONS, SINTERING CONDITIONS, AND DENSITIES OF THE TERNARY DISPERSOID SOLID-SOLUTION ALLOYS

Alloy	Nominal Dispersoid Alloy Content		Nominal Solid-Solution Alloy Content		Sintering Conditions		Alloy Density		
	Weight Per Cent	Volume Per Cent	Weight Per Cent	Atom Per Cent	Time, hr	Temperature, C	Theoretical(a), g/cm^3	Per Cent of Theoretical	
								Initial(b)	Final
WSD-1	1.1ThO_2·0.2Na_2O	2ThO_2	5.06Re	5.00Re	2	2600	18.95	56.0	94.0
WSD-2	2.2ThO_2·0.2Na_2O	4ThO_2	5.06Re	5.00Re	2	2600	18.90	54.7	92.3
WSD-3	4.4ThO_2·0.2Na_2O	8ThO_2	5.06Re	5.00Re	2	2600	18.50	50.3	83.4
					2	2600		83.4	87.0
					2	2800		87.0	89.8
WSD-4	4.4ThO_2·0.2Na_2O	8ThO_2	1.05Os	1.02Os	2	2600	18.50	49.8	90.1
WSD-5	4.4ThO_2·0.2Na_2O	8ThO_2	0.31Ir	0.30Ir	2	2600	18.50	49.3	87.0
					2	2600		87.0	95.5

(a) Calculated using the relationship $\frac{1}{d} = \frac{wt\%\,A}{100d_a} + \frac{wt\%\,B}{100d_b} + \ldots$, where d values for ThO_2, Na_2O, W, Re, Os, and Ir were taken as 10.03, 2.27, 19.30, 21.04, 22.57, and 22.5 g/cm^3, respectively.

(b) Refers to density achieved after pressing under 50,000 psi and presintering for 2 hours in a dry hydrogen atmosphere.

Vickers hardness data from these alloys are summarized in Table 24. Softening curves were constructed as shown in Figure 32. As can be seen from this figure, the shapes of the curves were generally similar. Both of the W-5.00Re alloys containing 2 and 4 volume per cent thoria recrystallized to hardness levels ranging from 43 to 66 VHN softer than those of unalloyed tungsten. Although the as-wrought hardnesses of both the W-1.02Os and W-0.30Ir alloys containing 8 volume per cent thoria were considerably higher (33 to 56 VHN) than that of unalloyed tungsten, the alloys recrystallized to hardness levels nearly equivalent to that achieved for unalloyed tungsten. The initially high hardness levels in these two alloys resulted from a combined effect of large dispersoid content (8 volume per cent) and increased strain-hardening tendencies associated with the dilute solid-solution-alloy additions. Even though only equivalent to unalloyed tungsten, the fully recrystallized hardness values showed softening which ranged from 37 to 27 VHN when compared with an 8 volume per cent thoria dispersoid alloy base.

The beginning and finish of recrystallization are denoted on each curve in Figure 32 by S and F; a summary of these data is presented in Table 25. For unalloyed tungsten the temperature range for 1-hour recrystallization spanned 200 degrees between 1400 C(S) and 1600 C(F), while each of the alloys recrystallized over a similar 200-degree interval between 1600 C and 1800 C. From this it was concluded that the general effect of the combined dispersoid and solid-solution additions was to increase the 1-hour recrystallization temperature through raising both the starting and finishing temperatures.

The grain size of each recrystallized microstructure was determined, and the grain sizes are reported in Table 26. Figure 33 illustrates the effect of increasing annealing temperatures on the resulting grain sizes of the four dispersoid-solid solution alloys. As shown, the slope of each curve in this figure is essentially the same; thus, none of the materials showed significantly different rates of grain growth from unalloyed tungsten. Each of the four alloys did, however, recrystallize to appreciably finer initial grain sizes than those of unalloyed tungsten. In all cases, the resultant wrought and recrystallized grain structures of the dispersoid-solid solution alloys were all very similar to those obtained for the dispersoid alloys. Table 27 compares the minimum recrystallized grain sizes achieved in the group of dispersoid-solid solution alloys with those obtained for the separate dispersoid and solid-solution alloying additions making up the more complex ternary materials.

It is significant to note that the finest grain sizes in the binary and ternary alloys containing thoria and rhenium were achieved in the ternary thoriated rhenium alloys, despite the fact that the rhenium-containing alloys received an additional high-temperature anneal during processing. Taken collectively, the data of Table 27 indicate that the separate grain-refining effects of dispersoid and metallics as binary additions are additive in ternary combinations.

Bend Transition Temperature

Individual bend specimens were cut from each of the four as-wrought ternary alloys and prepared according to the procedure previously described for the dispersoid alloys. Smooth bright surfaces resulted for both of the W-5.00Re base alloys after electropolishing. However, the same treatment applied to the W-1.02Os and W-0.30Ir alloys, each containing 8 volume per cent thoria, yielded badly pitted surfaces similar to and consistent with the surface condition of the binary W-Os and W-Ir alloys after polishing.

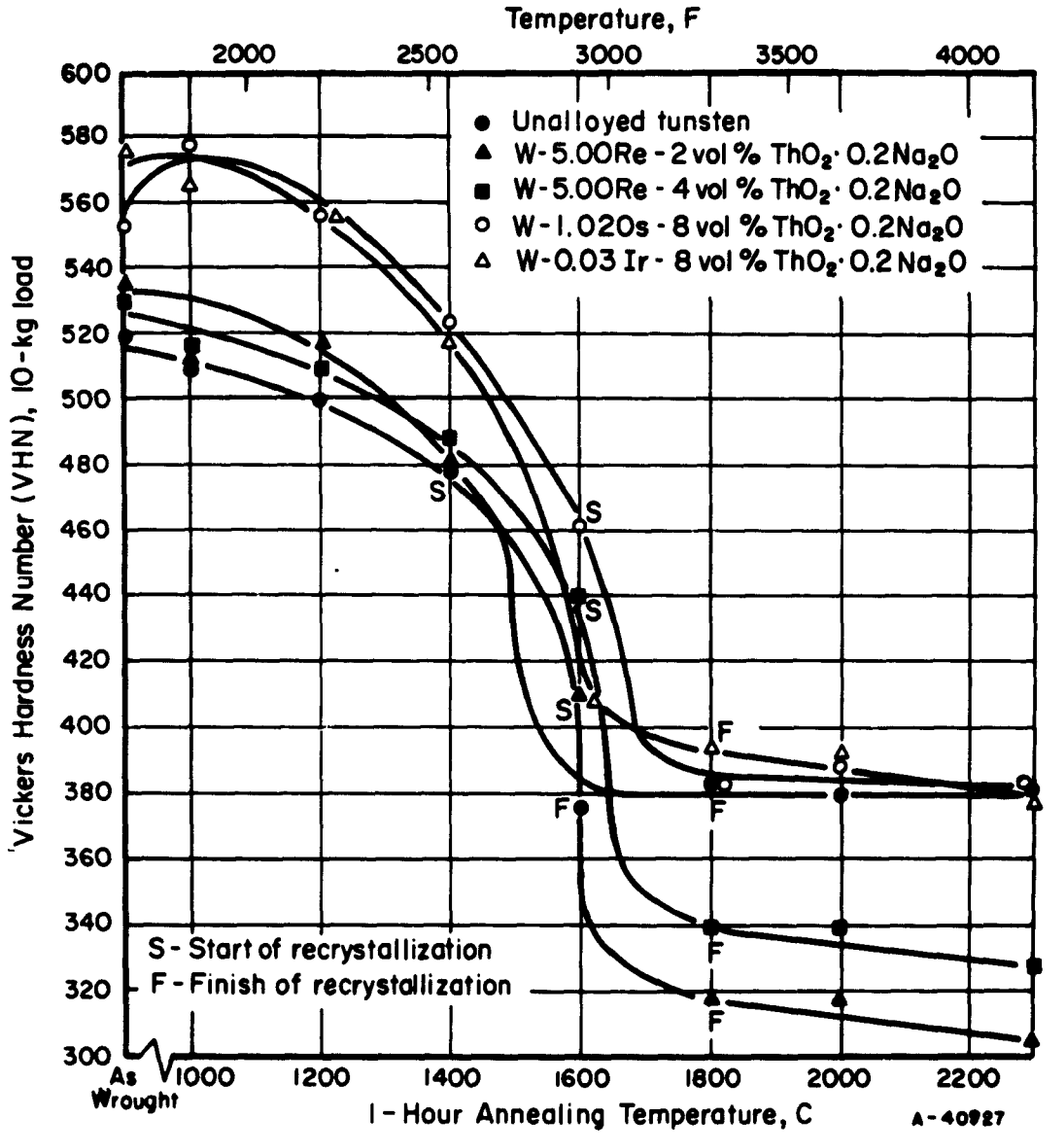


FIGURE 32. SOFTENING CURVES FOR WROUGHT UNALLOYED TUNGSTEN AND THE FOUR DISPERSOID-SOLID SOLUTION ALLOYS

TABLE 24. EFFECT OF ANNEALING ON THE MICROHARDNESS OF UNALLOYED TUNGSTEN AND THE DISPERSOID-SOLID SOLUTION ALLOYS

Alloy	Nominal Dispersoid Content, Weight Per Cent	Nominal Dispersoid Content, Volume Per Cent	Nominal Solute Content, atom per cent	Vickers Hardness Numbers (VHN), 10-Kg Load; As Wrought, Rolled 1200 C	1-Hour Vacuum-Annealing Temperature, C: 1000	1200	1400	1600	1800	2000	2300
Unalloyed Tungsten											
W-5	0	0	0	519	508	499	479	376[a]	383[a]	380[a]	382[a]
Dispersoid-Solid Solution Alloys											
WSD-1	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	5.00 Re	534	510	516	480	409	317[a]	317[a]	304[a]
WSD-2	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	5.00 Re	530	525	509	488	440	340[a]	339[a]	327[a]
WSD-4	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	1.02 Os	552	577	556	524	461	383[a]	388[a]	382[a]
WSD-5	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0.30 Ir	575	564	556	518	408	394[a]	392[a]	376[a]

(a) Fully recrystallized microstructures.

TABLE 25. SUMMARY OF RECRYSTALLIZATION OBSERVATIONS MADE ON UNALLOYED TUNGSTEN AND THE DISPERSOID-SOLID SOLUTION ALLOYS

Alloy	Nominal Dispersoid Content, Weight Per Cent	Nominal Dispersoid Content, Volume Per Cent	Nominal Solute Content, atom per cent	1-Hour Recrystallization Temperature, C: Start (S)	Finish (F)	Recrystallization Range, ΔC
W-5	0	0	0	1400	1600	200
WSD-1	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	5.00 Re	1600	1800	200
WSD-2	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	5.00 Re	1600	1800	200
WSD-4	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	1.02 Os	1600	1800	200
WSD-5	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0.30 Ir	1600	1800	200

TABLE 26. SUMMARY OF RECRYSTALLIZATION TEMPERATURES AND THE EFFECT OF HIGH-TEMPERATURE ANNEALING ON THE GRAIN SIZE OF UNALLOYED TUNGSTEN AND THE DISPERSOID-SOLID SOLUTION ALLOYS

Alloy	Nominal Dispersoid Content: Weight Per Cent	Nominal Dispersoid Content: Volume Per Cent	Nominal Solute Content, atom per cent	Approximate 1-Hour Recrystallization Temperature, C	Grain Size, grains/mm^2: 1-Hour Vacuum-Annealing Temperature, C: 1600	1800	2000	2300
Unalloyed Tungsten								
W-1	0	0	0	1600	1000	1175	650	--
W-4	0	0	0	1600	975	1150	775	175
Dispersoid-Solid Solution Alloys								
WSD-1	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	5.00Re	1800	--	4100	2350	1875
WSD-2	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	5.00Re	1800	--	5500	4625	3100
WSD-4	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	1.02Os	1800	--	5600	3400	2425
WSD-5	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0.30Ir	1800	--	6000	4850	3900

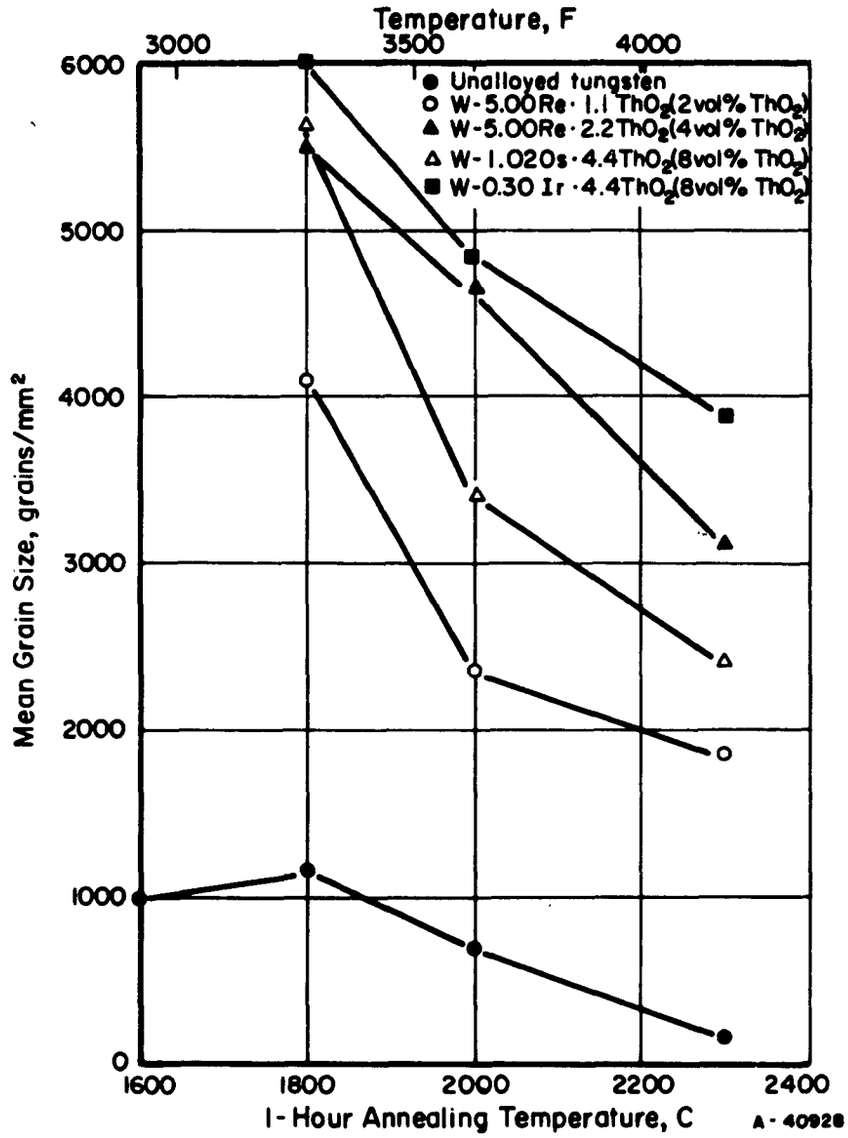


FIGURE 33. GRAIN-GROWTH BEHAVIOR OF UNALLOYED TUNGSTEN AND THE DISPERSOID-SOLID SOLUTION ALLOYS

TABLE 27. COMPARISON OF THE MINIMUM RECRYSTALLIZED GRAIN SIZES ACHIEVED IN THE TERNARY ALLOYS WITH THOSE OBTAINED FOR THE SEPARATE DISPERSOID AND SOLID-SOLUTION ALLOYS

Alloy	Nominal Dispersoid Content, Weight Per Cent	Nominal Dispersoid Content, Volume Per Cent	Nominal Solute Content, atom per cent	Minimum Recrystallized Grain Size, grains/mm^2
		Unalloyed Tungsten		
W-1 and W-4	100W	100W	100W	1162[a]
		Tungsten-Rhenium-Thoria		
WS-9	0	0	5.00Re	1775
WD-11	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	0	1450
WD-12	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	0	2900
WSD-1	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	5.00Re	4100
WSD-2	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	5.00Re	5500
		Tungsten-Osmium-Thoria		
WS-11	0	0	1.02Os	4000
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0	6800
WSD-4	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	1.02Os	5600
		Tungsten-Iridium-Thoria		
WS-12	0	0	0.30Ir	4200
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0	6800
WSD-5	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0.30Ir	6000

(a) An average of two values

Table 28 summarizes the ductile-to-brittle bend-transition-temperature tests conducted on the dispersoid-solid solution alloys. In this table comparisons are made between the ductilities of the ternary alloys and those of the separate binary dispersoid and solid-solution alloys which were combined to form the ternary alloys.

The data presented in Table 28 again illustrate that the beneficial effects of both the dispersoid and solid-solution components as separate binary additions are accumulative in ternary combinations. In each case, the combined additions of rhenium, osmium, or iridium with thoria gave significantly lower transition temperatures than were obtained with either the metallic or thoria additions alone. This was true for the alloys in both the stress-relief annealed and recrystallized conditions. The greatest decreases in transition temperature were obtained in the stress-relief-annealed osmium-thoria and iridium thoria alloys which contained the largest amount of dispersoid, i.e., 8 volume per cent thoria. Here, a common transition temperature of 75 C was obtained, which represents a reduction of 125 C in the transition temperature of the unalloyed tungsten control.

The effectiveness of increasing dispersoid content is illustrated by the comparisons below:

Alloy Combination	8T Transition Temperature, C	
	Annealed at 1200 C	Annealed at 1800 C
No addition	200	400
5.00Re	165	295
5.00Re + 2 vol % ThO_2	150	250
5.00Re + 4 vol % ThO_2	85	225

From this work it is apparent that the transition temperatures achieved in the W-5.00Re - 4 volume per cent ThO_2 alloy are almost as equally attractive as those achieved in the thoriated osmium and iridium alloys.

CONCLUSIONS

The important conclusions resulting from this investigation are summarized as follows:

(1) Fine dispersions of thoria and zirconia can be obtained in tungsten-metal powder through use of aqueous solutions of $Th(NO_3)_4$, $Zr(SO_4)_2$, or a 0.01-micron ZrO_2 sol. Densification of compacts containing these additions during sintering is greatly facilitated by first baking the loose powders at 600 C in hydrogen to remove as much of the gaseous decomposition products of $Th(NO_3)_4$ and $Zr(SO_4)_2$ as possible.

(2) Fine dispersions of thoria and zirconia had approximately an equivalent effect, on a volume per cent basis, on the fabricability, transition temperature, and recrystallization behavior of tungsten.

(3) For the bar size and rolling conditions used, 8 volume per cent of thoria or zirconia was about the maximum amount of oxide commensurate with good fabricability to 0.035-inch-thick sheet.

TABLE 28. SUMMARY OF DUCTILE-TO-BRITTLE BEND-TRANSITION-TEMPERATURE DATA ILLUSTRATING THE COMBINED EFFECTS OF DISPERSOID AND GROUPS VII AND VIII METAL ADDITIONS ON THE DUCTILITY OF TUNGSTEN

Alloy	Nominal Dispersoid Content, Weight Per Cent	Nominal Dispersoid Content, Volume Per Cent	Nominal Solute Content, atom per cent	Annealed 1-Hour at 1200 C, 8T Transition Temperature, C	Annealed 1-Hour at 1200 C, 8T Transition Temperature, F	Annealed 1-Hour at 1800 C, 8T Transition Temperature, C	Annealed 1-Hour at 1800 C, 8T Transition Temperature, F
Unalloyed Tungsten							
W-5	100 W	100 W	100 W	200	392	400	752
Tungsten-Rhenium-Thoria							
WS-9	0	0	5.00 Re	165	329	295	563
WD-11	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	0	185	365	325	617
WD-12	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	0	150	302	300	572
WSD-1	$1.1ThO_2 \cdot 0.2Na_2O$	$2ThO_2$	5.00 Re	150	302	250	482
WSD-2	$2.2ThO_2 \cdot 0.2Na_2O$	$4ThO_2$	5.00 Re	85	185	225	437
Tungsten-Osmium-Thoria							
WS-11[a]	0	0	1.02 Os	210	410	>450	> 842
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0	110	230	275	527
WSD-4[a]	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	1.02 Os	75	167	--	--
Tungsten-Iridium-Thoria							
WS-12[a]	0	0	0.30 Ir	> 400	> 752	>450	>842
WD-13	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0	110	230	275	527
WSD-5[a]	$4.4ThO_2 \cdot 0.2Na_2O$	$8ThO_2$	0.30 Ir	75	167	--	--

(a) Badly pitted after electropolishing.

(4) Thoria and zirconia inhibit grain growth in tungsten during sintering and rolling and also increase the recrystallization temperature of the wrought product.

(5) Increasing amounts of thoria and zirconia are increasingly effective in decreasing the bend transition temperature of tungsten in both the stress-relief annealed and recrystallized conditions.

(6) The low-temperature bend ductilities of wrought tungsten and tungsten-base dispersoid sheet alloys vary with the stress-relief-annealing conditions used. For alloys containing 8 volume per cent thoria or zirconia, bend transition temperatures as low as 85 C to 90 C can be obtained.

(7) The beneficial effects of thoria and zirconia on the properties of tungsten primarily result from grain-size control.

(8) Small binary additions of Groups VII and VIII metals to tungsten decrease its hardness. The magnitude of the softening obtained is greatest for elements of the third long period, which includes rhenium, osmium, and iridium.

(9) The preparation of homogeneous binary alloys of tungsten with Groups VII and VIII metals by powder-metallurgical techniques is facilitated by using fine metal powders and careful blending prior to compaction. Alloys of W-5.00Re, W-0.87Os, and W-0.30Ir can be rolled to good quality 35-mil-thick strip using procedures similar to those for the W-ThO_2 and W-ZrO_2 alloys.

(10) Small (5 per cent or less) binary additions of rhenium, osmium, and iridium to tungsten are effective in lowering its ductile-to-brittle bend transition temperature, increasing its recrystallization temperature, and reducing its recrystallized grain size.

(11) The beneficial effects of small additions of rhenium, osmium, and iridium are primarily ascribed to the decreasing of the solubility limit of tungsten for interstitial impurities.

(12) Small additions of rhenium, osmium, or iridium to thoriated tungsten powder compacts tend to inhibit densification during sintering. Also, breakdown rolling conditions for such ternary alloy combinations containing 8 volume per cent thoria are more critical than for binary thoria alloys alone.

(13) The beneficial effects of additions of thoria, rhenium, osmium, and iridium on the transition temperature and grain size as binary additions appear to be additive in ternary combinations. Thus, combined additions of 2 to 8 volume per cent thoria with 5 per cent rhenium, 0.87 per cent osmium, or 0.30 per cent iridium are effective in lowering the transition temperature of tungsten from 200 C to 75 C to 85 C, increasing its recrystallization temperature by 200 C, and decreasing its recrystallized grain size.

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